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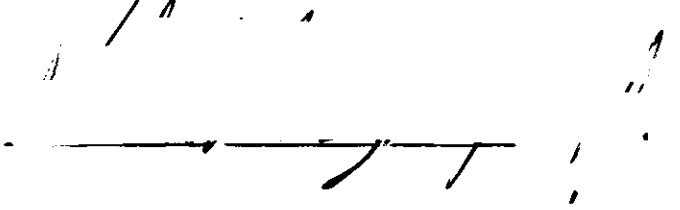

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STUDIES IN PHOTOMETRIC ANALYSIS INCLUDING DESIGN AND CONSTRUCTION OF A FULL-IMMERSION PHOTOMETER

A THESIS

Presented to

The Faculty of the Graduate Division

by

Robert Milton Speights, Jr.

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STUDIES IN PHOTOMETRIC ANALYSIS INCLUDING DESIGN AND CONSTRUCTION OF A FULL-IMMERSION PHOTOMETER

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SUMMARY

In the present study, kinetic masking (i.e., masking via formation of complexes which are slow to react) is utilized in the photometric determination of cobalt in high purity nickel. To facilitate the study of the kinetics of the chemical system, a total immersion photometer was designed and constructed. The instrument has proved to be a versatile photometer, and to satisfy the special requirements for a photometrator.

Determination of Trace Cobalt in Nickel

Cobalt can be determined photometrically as the green Co(III)-PAN chelate in high purity nickel in the following manner. The sample is dissolved in 1:1 HNO_3, the solution neutralized with ammonia and adjusted to pH 10 with ammonia-ammonium chloride buffer. The total metal (nickel plus cobalt) is titrated in warm solution to a murexide end point with EDTA. After cooling to room temperature or below, the pH is adjusted to about 2 and bismuth nitrate solution is added. The bismuth rapidly displaces cobalt from its EDTA complex, but nickel is slow to react and remains as the EDTA complex throughout the remainder of the procedure. Ethanol is added until a 50 per cent ethanol-water solution is obtained. PAN is added and the solution allowed to stand for an hour. Then the Co(III)-PAN complex formed and the excess PAN are extracted into chloroform, and the absorbance of the extract is measured at 625 nm. Accurate results have been obtained for Ni:Co ratios up to 1,000,000. The effect

of the presence of potentially bothersome metals (in particular iron and copper) has been investigated and procedures established to eliminate their interference.

Design and Construction of an Immersion Photometer

A simple yet versatile total immersion photometer is described. The design provides for operation in ambient light without special cuvettes, and allows continuous adjustment of the pathlength without changing vessels. Operation in ambient light is achieved by utilizing the principle of geometric exclusion. Constructional details are given as well as operational procedures.

Application of the instrument to rate studies in cooled solutions is discussed.

Use of the instrument as a phototitrator is discussed. One special feature of particular importance to photometric titrations is the capacity for scale expansion beyond 100 and by zero suppression. This feature is discussed and instructions for instrument programming are given.

CHAPTER I

INTRODUCTION

Spectrophotometry

The absorption of radiation by molecular species has long been used by analytical chemists for the quantitative determination of the concentration of the absorbing species. The wide acceptance of the techniques based on measurement of such absorption can be attributed to the great variety of determinations possible, to the high sensitivity of many of these, to the low cost of the instrumentation required, and to the simplicity of the operation of these instruments.

One of the primary advantages of spectrophotometric analysis is that trace quantities of many substances can be determined. A large portion of presentday trace analyses are accomplished utilizing either emission spectrography or absorption spectrophotometry. Emission spectrography shows itself to best advantage in the analysis of many samples of approximately identical gross composition. It is useful for determining many elements, but with widely varying sensitivity. Considerable work is required in calibration, but isolation of the determined element is not required. Absorption spectrophotometry likewise, finds a wide range of application, but most cases require some degree of isolation of the element to be determined, which is a source of both weakness and strength. Separations are not always possible, and are almost never easy. However, for the many systems for which separation can be achieved,

the absorption spectrophotometric determination becomes an absolute one in that it is independent of matrix effects. The emission spectrophotometric method generally has a higher absolute sensitivity, but the much larger sample which can be used in the absorption spectrophotometric technique leads to comparable lower detection limits.

Absorption of Radiation

The wave theory of light explains many of the optical properties of light, but others, such as molecular absorption, are best interpreted in terms of the concept of light "particles". Such "particles" are not particles at all, but are described best as packets of energy, and are called photons. Light of a given frequency, ν, is associated with photons of an energy, E, given by

$$E = h\nu \qquad (1)$$

where h is Plank's constant.

A molecule can be regarded as having two different kinds of energy: kinetic (translational) and potential. Absorption of light by a molecule occurs only if the interaction between photon and molecule leads to a charge separation. Direct interaction between light and the translational energy of a molecule is thus precluded, and exchange can only involve interaction of a photon with the potential energy of the molecule.

Since the potential energy of a molecule is quantized, changes in potential energy for a molecule may involve only certain discrete energy values. Electromagnetic radiation of a specific frequency is associated with each such energy value (Equation 1). Molecular absorption spectra

should thus be characterized by absorption at specific frequencies characteristic of the molecular system. The qualitative information gained by study of the frequencies at which absorption occurs can be used in characterizing the molecular system. The infrared region of the spectrum is the most used in this regard.

The visible and near ultraviolet regions of the spectrum have been most utilized in quantitative procedures. The energy of photons in the visible and ultraviolet regions (ca, 100kcal./mole) corresponds to that associated with an electronic transition within a molecule. The discrete line absorption spectra expected for a molecule interacting with light energy in one of these regions are not observed because the large number of vibrational and rotational states possible for each electronic level, and the energy associated with each of these, makes possible many transitions of nearly identical energies. The closely spaced abosrption lines are seldom resolved, and the absorption associated with an electronic transition becomes an absorption band. In the restricted visible and ultraviolet regions, the effect of broadened absorption bands is a reduction in the number of bands that can be accommodated without considerable overlap. This fact leads at once to a restriction on the selectivity of absorption spectrophotometric techniques aside from any selectivity considerations normally associated with reagents or reactions. To cope with problems created by this overlap for analytical purposes requires either complicated, and often unsatisfactory, mathematical analysis, or isolation of the absorbing species of interest.

Laws of Spectrophotometry

When a beam of monochromatic radiation traverses a homogenous layer of a substance, absorption occurs if the frequency of the radiation corresponds to the energy required to elevate the system to a higher energy state in an allowed transition. Spectrophotometry is based on the relationship which has been shown to exist between the absorption of light and the absorbing media. Two laws have been formulated to describe the quantitative aspects of this relationship. The Bouguer or Lambert Law states that when a beam of parallel monochromatic radiation is passed through an absorbing media, the power of the transmitted radiation decreases in an exponential fashion as the thickness of the absorbing medium increases arithmetically. Bouguer's finding may be expressed mathematically as follows

$$-\frac{\partial P}{\partial b} = k'P \qquad (2)$$

where P is the radiant power of the light beam, b is the thickness of the layer, and k' is a proportionality constant. Integrated between the limits of 0 and b, and P_o and P, the expression becomes

$$-\ln \frac{P}{P_o} = k'b \qquad (3)$$

where P_o is the radiant power of the incident beam and P is the radiant power of the emergent beam. This law is strictly applicable only to monochromatic radiation.

The relationship between the concentration of light absorbing species and the extent of absorption is known as Beer's Law. Beer's Law

is identical in form to Bouguer's Law in describing an exponential decrease in transmitted radiant power with an arithmetic increase in concentration of absorbing species. The law may be expressed mathematically as

$$-\frac{\partial P}{\partial c} = k''P \tag{4}$$

where c is the concentration of the absorbing species, and k" is a proportionality constant. In integrated form the expression may be written

$$-\ln\frac{P}{P_o} = k''c \tag{5}$$

The two laws can be readily combined to give a convenient expression relating changes in transmitted radiant power to changes in both pathlength and concentration. This expression, known as the Beer-Lambert Law can be written in the form

$$-\ln\frac{P}{P_o} = Kbc \tag{6}$$

where K is a combination of the earlier proportionality constants. The Beer-Lambert Law is most often written using ordinary (base 10) logarithms. It then appears as

$$\log\frac{P}{P_o} = -abc \tag{7}$$

The proportionality constant, a, is termed absorptivity and is normally given in units of liters/gm·cm. The transmittance, T, is conventionally

defined* as the ratio of the radiant power transmitted by a sample to the radiant power incident on the sample. The negative logarithm of T is called the absorbance, A. Incorporation of these definitions yields

$$- \log \frac{P}{P_o} = - \log T = A = abc \qquad (8)$$

This is the most common form of the Beer-Lambert Law. Concentration of the absorbing species is used in grams per liter. Should the concentration c be expressed in moles per liter, the proportionality constant is termed the molar absorptivity and given the symbol ε (liters/mole · cm). In any case, the proportionality constant is a function of the identity of the absorbing species, the frequency of the light, the nature of the solvent and other factors.

Determination of Absorbance

The determination of absorbance always involves the comparison of two luminous intensities. The techniques for accomplishing this comparison are varied including visual, photographic, and photoelectrical cell methods. Only the latter is currently of significant analytical importance.

Various types of apparatus can be utilized for the determination of the ratio P/P_o. Single beam deflection instruments represent the simplest approach. In instruments of this type, the deflection of a current meter or galvanometer is adjusted to the 100th division for a

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*The terms, symbols, and definitions set forth here are those suggested by the advisory board of Analytical Chemistry[1]

current i_o generated in the detector by P_o. The reading of the meter when P is incident on the detector gives the transmittance ($T = P/P_o$) as a percentage.

Single beam null instruments use a calibrated current to compensate for the change in current caused by the replacement of P_o with P. The magnitude of the current required to achieve null is related to the transmittance. Null design can also be used in double beam instruments. The detection technique is the same as with single beam design, but the comparison is simultaneous. Optical compensation can also be used, utilizing a device such as an optical wedge or shutter which is placed in the path of the light beam. This type compensation is used most in double beam instruments.

The Photometric Error

The photometric error in an analysis is the error in the computed concentration which results from the instrumental error in the absorbance measurement. If the error in the concentration is expressed in terms of the deviation, Δc, from the true concentration c, the relative error in c will be $\Delta c/c$.

A clear indication of the nature of the error in concentration is gained by writing an expression for the relative error in terms of the uncertainty in evaluation of the photodetector current. This uncertainty ultimately corresponds to an uncertainty ΔI in the measurement of the intensity of the light. Thus from Beer's Law

$$\Delta A = ab\Delta c = - 0.434 \frac{\Delta P}{P} \qquad (9)$$

where P is the radiant power of the emergent beam. From which

$$\Delta c = \frac{-0.434}{ab} \frac{\Delta P}{P_o} \ 10^A. \tag{10}$$

P_o is the intensity of the incident beam. Thus

$$\frac{\Delta c}{c} = \frac{\Delta A}{A} = - \ 0.434 \ \frac{\Delta P}{P_o} \ \frac{10^A}{A}. \tag{11}$$

The ratio $\Delta P/P_o$ expresses the relative error in determining the light intensity. The experimental accuracy will increase in proportion as the instrument permits $\Delta P/P_o$ to be as small as possible for any given wavelength. The minimum value of this ratio depends on wavelength, since P is related to the photodetector current error by a wavelength sensitive proportionality constant. An increase in P_o, the intensity of the light source, would seem desirable. However, if the intensity is too high, the photodetector will not respond to small variations in the intensity. When $\Delta P/P_o$ becomes sufficiently small, other causes of error predominate, and the above relations can no longer be considered representative of the actual error.

It can be seen by rewritting Equation 11 in terms of experimental variables as

$$\frac{\Delta c}{c} = 0.434 \ \frac{\Delta T}{T(\log T)} \tag{12}$$

that for a given value of ΔT corresponding to a given error in determining the light intensity, the error depends only on the value of T. If the error in transmittance, ΔT, is 1 per cent, absolute, the relative error

in concentration varies with transmittance as shown in Figure 1.

Several other errors can be attributed to instrumental origin. Perhaps the most important of these is non-linearity of the photodetector and output device. Apparent deviation from Beer's Law is observed if the photodetector current is not directly proportional to the intensity of the light striking the detector. Deviations are also observed if any current amplification employed is non-linear. The error introduced by stray light must also be considered. This error is most pronounced when light levels at the detector are low as is the case when the radiant power of the emergent beam is low. Variations in the intensity of the light source will also generate errors. This source of error can be minimized by careful regulation of the lamp supply voltage, and nearly eliminated by double beam operation. Changes in temperature of the photodetector or the optics of an instrument should be considered as well.

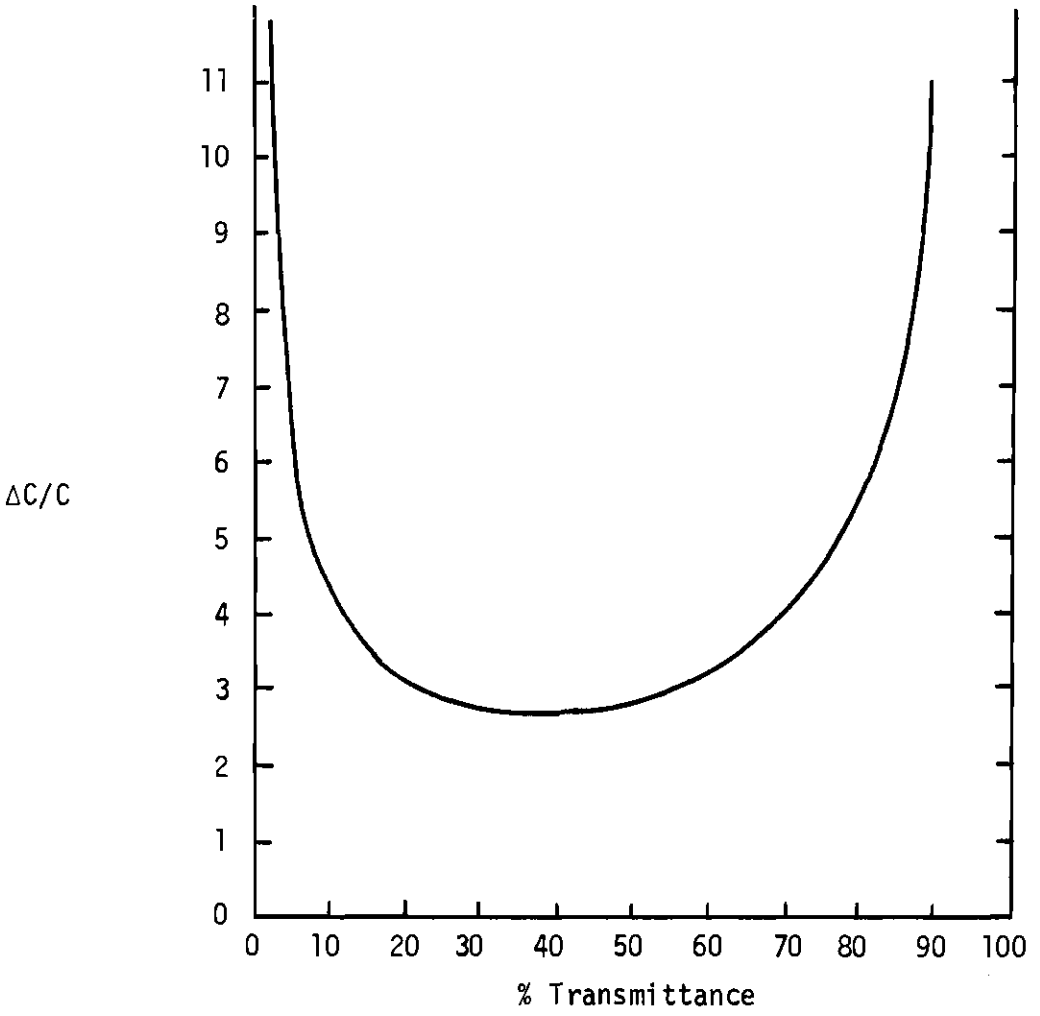


Figure 1. The Relative Error in Concentration as a Function of Transmittance, for Unit Photometric Error ($\Delta\%T = 1$).

CHAPTER II

SPECTROPHOTOMETRY IN TRACE ANALYSIS

General Requirements

Several desiderata are noted when minute amounts of a substance are to be determined. Certainly the two most important of the factors to be considered are sensitivity and selectivity. For a highly sensitive and selective color reaction, some other characteristics are also desirable. These include simplicity, speed, reproducibility, stability of color, ruggedness, and adherence to Beer's Law. Any of these will be sacrificed for sensitivity gains.

The special aspects of several of these factors are discussed in the following sections.

Sensitivity

In spectrophotometric analysis knowledge of the sensitivity of the color reaction employed is of paramount importance. Sandell[2] has suggested that the sensitivity of a color reaction be defined as the smallest weight of a substance that can be detected in a column of unit cross-section. This sensitivity is most often expressed in micrograms per square centimeter. He further points out that there are two factors involved in the sensitivity related to (1) the absorptivity of the colored product, and (2) the ability of the observer to detect small differences in the transmittance of the sample. The minimum amount of a colored sub-

stance that can be detected is not normally established by the sensitivity of the photoelectric detector. The limit depends, rather, on the ability of the detector to reproducably differentiate between the transmittances of two solutions, one the blank and the other the faintly colored sample solution. A reasonable basis for the expression of sensitivity may be established by assuming that a photoelectric spectrophotometer can detect with certainty a difference of 0.001 in absorbance. This corresponds to a difference of 0.2 per cent in the transmittances of blank and sample and is reasonable in light of the performance of commercially available instruments.

Examination of the Beer-Lambert Law suggests two approaches to increasing the sensitivity (lowering c) within the instrumental limit of 0.001 absorbance units. Sensitivity would certainly be enhanced by development of reagents which yield highly colored species for determination. This approach would increase the numerical value of a, and the "intrinsic" sensitivity. Braude[3] has shown that the maximal value of molar absorptivity theoretically obtainable is of the order of 100,000.

An alternative approach to increasing sensitivity suggested by the Beer-Lambert Law is to increase the signal for a given concentration by increasing the value of the pathlength, b. The difficulties associated with longer pathlength increase in proportion. Light scattering, internal reflections, stray light, instrument alignment, and reagent absorption, among others, become factors contributing significantly to the uncertainty in the measured transmittance.

The outcome of these considerations is the appearance of a sensi-

tivity barrier for spectrophotometric determinations. The location of this barrier can be expressed in terms of the concentration of absorbing species. For an absorbance of 0.001 units, a molar absorptivity of 100,000, and a pathlength of one centimeter the Beer-Lambert Law yields the value of that concentration as

$$A = a \times b \times c$$

$$0.001 = (100{,}000 \ \frac{\text{liter}}{\text{mole cm}})(1 \text{ cm})(c \ \frac{\text{moles}}{\text{liter}}) \qquad (13)$$

Solution of this equation for c yields a value of 1×10^{-8} moles/liter. This is 1×10^{-11} moles per square centimeter for a one centimeter pathlength. Expressed in micrograms per square centimeter (Sandell sensitivity) this becomes

$$(MW \ \frac{g}{\text{mole}})(10^6 \ \frac{\mu g}{g})$$

$$S = (1 \times 10^{-11} \ \frac{\text{moles}}{cm^2})(MW \times 10^6 \ \frac{g}{\text{mole}}) = MW \times 10^{-5} \ \frac{\mu g}{cm^2} \qquad (14)$$

where MW is the molecular weight of the absorbing specie. In practical analysis, the molecular weight of the species of interest is substituted for that of the absorbing species. This is possible because of the stoichiometric relation between the two species. Consider, for example, the determination of a metal of molecular weight 100, which forms a 1:1 complex with the chromogenic agent. If a one gram sample is used, and the colored species is developed in a final volume of 25 ml, the minimum detectable amount of the metal is $(10^{-8} \ \frac{\text{mole}}{\text{liter}})(0.025 \text{ liter})(100 \text{ gm/mole}) = 2.5 \times 10^{-8}$ gm or 0.025 parts per million.

Common values for the molar absorptivity of species induced in the more sensitive practical methods lie in the range 10,000 - 40,000. Thus, the detectable limit is normally somewhat less than the ideal case described above. The situation can be improved by reducing the solution volume or increasing the pathlength, but the difficulties associated with these steps frequently outweigh the potential gain. In practical analysis 0.1 ppm of many elements can be determined in a one gram sample assuming appropriate separations are feasible, but to extend the limit to 0.01 ppm is not practical under the conditions assumed.

Selectivity

In trace analysis selectivity is second only to sensitivity in importance. Selectivity can be achieved via instrumental or chemical means, or more often both. Proper choice of wavelength provides instrumental selectivity. Chemical selectivity is accomplished by proper choice of conditions and reagents for the production of a single colored species characteristic of the sought-for element.

Even though most reagents do not *per se* react selectively, often they can be made to do so by masking. The term masking is used to describe the process of preventing an undesirable reaction without physically separating any species from the solution. Masking can be accomplished by precipitation, oxidation or reduction, complexation, pH adjustment, or kinetically by temperature control. The most widely applied masking technique is complexation. If a solution of two metals, for example, is treated with a reagent which forms a stable complex with only one of the two, and if the second metal can then be reacted selectively

with a chromogenic reagent, the first metal is said to have been masked.

In many practical cases involving masking, several of the masking techniques are simultaneously employed. If the masking fails to provide sufficient selectivity, a separation may be required.

Physical separation techniques including precipitation and filtration, ion exchange, chromatography, solvent extraction, and others have been utilized. Two approaches are available. The desired constituent may be removed from its matrix alone, or the bulk of the interfering species may be removed leaving behind the species of interest in a relatively pure form. In many cases a separation can be combined with one type of masking resulting in an enhancement of overall selectivity and a reduction in the required efficiency of each technique.

Accuracy and Precision of Absorption Spectrophotometry

The precision demanded of colorimetric methods, as all analytical methods, depends on the ultimate purpose of the analysis. In trace analysis it is often acceptable to determine an element with a relative error of 10, 20 or even 100 per cent. For indeed, it is better to determine the order of magnitude of a trace element than to be unable to make any quantitative estimate of it. Each component of an analytical procedure, including the instrument and the experimenter, has its own scatter; commonly, the worst of these sources of error determines the overall error of the system.* To a large extent the precision of a procedure is proportional to the ingenuity and energy of the experimenter.

*For a collection of uncertainties ($\Delta_i D$) of the same order of magnitude, the overall uncertainty (ΔD) resulting from their simultaneous presence is given by $\Delta D = (\Sigma_i D)^2$. Thus only a slight difference between them is necessary for one of them to become preponderant.

As far as accuracy is concerned, errors in absorption spectrophotometric methods can be considered to be of three kinds (1) Errors having their origin in the color forming process, (2) those errors due to foreign substances, and (3) those errors associated with the process of measurement of color intensity.

The conditions in a color reaction for quantitative purposes must be amenable to control such that virtually constant amounts of the colored product are formed from constant amounts of the constituent to be determined. Several experimental variables almost invariably demand close control. If, for example, a chemical equilibrium is involved, dilution may shift the equilibrium. The total concentration of absorbing substance may thus be reduced to a greater extent than would be predicted from consideration of dilution alone. Changes in pH may also have a pronounced effect on such equilibria. This occurs because most chromogenic reagents used in developing a color for photometric analysis are also acids or bases. Changes in the pH of solutions of such reagents may considerably alter the degree of complexation and cause serious errors in the determination. Solvent composition must be controlled. Losses in light intensity due to reflection are related to the difference in refractive indexes of two media forming an interface. Beer's Law, as it is generally stated, is the limiting case of a more exact relation

$$- \log \frac{P}{P_o} = \frac{n\ 0.434}{(n^2 + 2)^2 (k''c)^{-1}} \qquad (15)$$

in which n is the refractive index of the solution.[4] This expression

accounts for the reflection loss at the solution interface as a function of the refractive index, and indicates the need for constant n in a series of measurements. Other variables which may require close control include the excess of the reagent, the time of standing before the color intensity is measured, and the temperature of color development.

The systematic variations described above are frequently termed deviations from Beer's Law. It should be noted that these deviations are not real, but are apparent. Perhaps the only "true deviation" from Beer's Law which has been described is the "neutral salt effect." This effect accounts for the interaction of an absorbing species with its environment. The existence of this deviation points up the need for consideration and control of foreign substances. In trace analysis small errors may result from the presence of electrolytes in high concentration.

Beer's Law is strictly applicable only to monochromatic light. Any instrumental factor which contributes to the non-monochromaticity of the light will have an adverse effect on the measurement of absorbance. One particularly important factor is that of stray light. It should be excluded to the greatest possible extent. Non-reproducibility in setting the proper wavelength can also lead to a systematic error. Care must be taken in the selection of wavelength for the determination, and in the instrumental setting of that wavelength.

Precision Photometry

In an earlier section the photometric error was evaluated on the assumption that the controlling source of error could be identified as the instrumental error. This is normally the case unless the chemical

procedure entails some extraordinarily imprecise step. The factors contributing to the instrumental error are the uncertainties in the phototube current, the linearity of amplification, fluctuations in the light source, and errors in the response, and reading of the output meter. The uncertainties attributable to the meter generally overshadow other errors. Having identified the prime contributor to the photometric error it is advantageous to consider reducing the magnitude of its uncertainty.

The influence of errors associated with uncertainties in the response and reading of the output meter can be reduced by expanding the scale. The improvement reaches limit when the error associated with the output reaches a level comparable with errors from other sources. The scale expansion is accomplished by proper selection of the reference solutions chosen to correspond to the ends of the instrument scale.

Four possibilities have been elucidated and the errors associated with each evaluated by Reilley and Crawford.[5] The basic assumption associated with the evaluation is that the reading error, ΔT, is constant. Under this assumption the photometric error is proportional to an error coefficient characteristic of the technique employed. The "ordinary" method employs darkness to establish the zero and pure solvent to set the upper limit of the scale (normally 100 divisions). The error coefficient is $1/T_s \ln T_s$. (The relation of this coefficient to the relative error can be seen from Equation 12). From the error curve (Figure 1) it can be seen that for ordinary (classical) photometry the optimum range for sample transmittance is from 20 to 65 per cent with the minimum occurring at 37 per cent.

In the "transmittance ratio" method, a solution of known concentration and with an absorbance lower than that of the solution to be analyzed is placed in the path of the light beam. The radiant power of the emerging beam is used to set 100 by increasing the amplification or the incident light intensity. The scale zero is again set with darkness as reference. This technique is useful for solutions of high concentrations of absorber. The error coefficient becomes $T_{su}/T_s \ln T_s$, entailing the transmittance of the reference, T_{su}, as well as that of the sample itself. An improvement in precision can be achieved if T_{su} is less than 50 per cent, and will increase as the sample transmittance approaches that of the reference.

In the "trace analysis" method the instrument is set to read 100 when the detector is exposed to light which has passed through pure solvent and to read zero when the detector is exposed to light which has passed through a reference solution somewhat more concentrated than the sample. The error coefficient becomes $1 - T_{sl}/T_s \ln T_s$, and again includes the transmittance of the reference solution, T_{sl}, but in this case the reference is for the lower end of the scale. A gain in precision will be achieved if T_{sl} is greater than 50 per cent, and if the scale reading is between 0 and about 65 division.

The "ultimate precision" method defined by Reilley and Crawford[5] is potentially the most precise of all the techniques. The instrument is set for both 0 and 100 using reference solutions. The error coefficient, $(T_{su} - T_{sl})/T_s \ln T_s$, shows a dependence on the difference between the transmittance of the two reference solutions.

The trace analysis method is of particular interest in the photo-

metric determination of trace elements. In such analyses, solutions frequently have transmittance greater than 80 per cent. The potential gain in precision by using the trace analysis method can be found by inspection. Consider, for example, the gain in precision associated with the replacement of the classical method with the trace analysis method when a reference of 80 per cent transmittance is employed. The numerator of the error coefficient for the latter method in this case is 1 - 0.80 = 0.20. This figure divided into the numerator of the error coefficient of the classical method gives 1÷0.20 = 5. This indicates a five-fold gain in precision. It is worth noting that the gain in precision depends only on the selection of the reference solutions.

It must be kept in mind that this improvement in precision is only valid as long as the initial assumption holds, that is, as long as other sources of error are small compared to the reading error. Substantially more precise results can be achieved in many cases.

CHAPTER III

EQUIPMENT AND CHEMICALS

Laboratory Equipment

Spectrophotometers

The absorbance curves were obtained with either a Bausch and Lomb Spectronic 505 or a Beckman Model DK recording spectrophotmeter. The analytical absorbance measurements were made with a Bausch and Lomb Spectronic 20. The qualitative survey experiments associated with the determination of cobalt discussed in Chapter IV were performed with the total immersion photometer described in Chapter V. Screen calibrations of the immersion photometer were made with a Cary Model 14 recording spectrophotometer.

pH Meter

All pH measurements were made with a Beckman Zeromatic II pH meter. This device was calibrated with a Beckman pH 4.01 buffer.

Glassware

The usual laboratory glassware such as beakers and flasks were used as needed. All volumetric Class A glassware was used without additional calibration.

Chemicals

Water

Deionized water was used exclusively.

1-(2-Pyridylazo)-2-naphthol (PAN)

Certified Reagent grade PAN from Fisher Scientific Company was used. A 0.01 F indicator solution was prepared by dissolving 0.622 gm of the solid material to 250 ml with 95 per cent ethanol.

Murexide

One gram of the solid Murexide Indicator Powder was thoroughly ground with 50 gm of reagent grade sodium chloride. J. T. Baker Reagent Grade Murexide and sodium chloride were used.

Disodium (Ethylenedinitrilo)tetraacetic Acid Dihydrate (EDTA)

Mallinckrodt Chemical Works "Analytical Reagent" disodium EDTA was used. A stock solution was prepared by slurrying about 108 g of disodium EDTA in about a liter of water. A few pellets of sodium hydroxide were added to hasten dissolution and the solution was diluted to two liters. The resulting solution was about 0.15 F. A seventy-five milliliter volume of this solution was diluted to one liter to make a 0.01 F solution which was standardized against a standard zinc solution.

Acids

DuPont concentrated nitric, hydrochloric, phosphoric, and sulfuric acids were used as required.

Bases

DuPont concentrated aqueous ammonia and J. T. Baker "Analysed" sodium hydroxide pellets were used as required.

Zinc Standard Solution

A standard 0.1000 F zinc solution was prepared by dissolving 6.538 gm of Baker "Analysed" zinc metal in the minimum amount of nitric

acid. The solution was then boiled briefly to expel oxides of nitrogen, cooled, and diluted to one liter.

Cobalt

A 0.1 F cobalt solution was prepared by dissolving 1.47 g of cobalt metal in a minimum amount of 1:1 nitric acid and diluting to 250 ml. A twenty milliliter volume of this solution was diluted to 500 ml and the resulting solution standardized against the 0.01 F EDTA solution. A direct titration was employed at pH 10 with murexide indicator for end point detection. Fifty milliliters of the 3.97×10^{-3} F solution standardized above was diluted to one liter giving a cobalt solution of 1.964×10^{-4} F in cobalt.

Nickel

A 2.0 F nickel solution was prepared by dissolving 59.46 gm of J. T. Baker nickel shot in a minimum amount of 1:1 nitric acid and diluting to 500 ml.

Bismuth

An approximately 0.1 F bismuth solution was prepared by dissolving 48.3 gm of bismuth nitrate in water to which several ml of concentrated nitric acid had been added, and diluting to one liter.

Other Metal Salt Solutions

J. T. Baker reagent grade metal salts were used to prepare the aqueous solutions. If the salt undergoes hydrolysis, a few drops of nitric acid were added.

Hydrogen Peroxide

Fisher Scientific reagent grade 30 per cent hydrogen peroxide was used.

Tartaric Acid

J. T. Baker reagent grade solid tartaric acid was used.

Buffer pH 10

J. T. Baker reagent grade ammonium chloride and duPont aqueous ammonia were used to prepare the buffer. Ammonium chloride (70 gm) and concentrated aqueous ammonia (570 ml) were combined and diluted to one liter.

Storage of Solutions

All chelon and indicator solutions, all alkaline solutions, and all dilute (0.001 F or less) metal ion solutions were stored in polyethylene bottles.

CHAPTER IV

DETERMINATION OF TRACE COBALT IN HIGH PURITY NICKEL

Introduction

Nickel was discovered and recognized as an element by A. F. Cronstedt at the Swedish Department of Mines in 1751.[6] Its importance industrially has increased steadily since that discovery. Parallel to this growth has been the development of the analytical chemistry of nickel. As is usually the case, the development of analytical techniques has been no faster than the demand for them, and frequently slower.

The recent demands of nickel technology have been for nickel of ever increasing purity. Compliance with this demand has required the evolution of analytical methods compatible with the new lower levels of impurity. The lower concentrations of impurity elements increases the difficulty of analysis.

One of the most serious problems of nickel analysis is the lack of standard samples. This situation is created by a dearth of analytical methods of sufficient accuracy and reliability to establish such. Again the need of improved analytical methodology precedes its development.

The method here developed is intended to provide a method of high accuracy and reliability for one impurity element - cobalt. The method will be found practical both for routine analysis and for use in establishing standards for other techniques.

Historical

In view of the close association of cobalt and nickel, it is not surprising that a large number of methods for the determination of cobalt in nickel have been published. Critical surveys of the commonly used methods have been published.[7,8]

Most gravimetric methods have used 1-nitroso-2-naphthol which was introduced by Ilinsky and von Knorre.[9] Modern modifications of this method are still advocated for general nickel analysis. Other gravimetric methods have been recently introduced; these shown no great advantage over the established method, and suffer from the same limitations in requiring a large sample.

Volumetric determination of cobalt in nickel by titration with ferricyanide has been studied by Hall and Young.[10] High purity nickel, however, contains too little cobalt for titrimetric analysis. Similar objections can be raised against the polarographic methods. The method[11] of Meites for the determination of cobalt(III) by reduction of the ammine complex was found suitable for the determination of 0.0065 per cent cobalt in nickel metal. Atomic absorption has been used for the determination of cobalt in nickel,[12] but due to the high salt concentration serious problems at the burner are encountered for samples with less than about 0.001 per cent cobalt. As little as 4 ppm cobalt has been determined by neutron activation analysis.[13] A high flux neutron source is required.

Emission spectrography is most useful for the simultaneous determination of several elements of low concentration in a matrix of known and nearly invarient composition. Analysis of high purity nickel offers

an ideal application. Rupp, Klecak, and Morrison[14] used a 14-ampere direct current arc in an argon atmosphere for the analysis of twelve elements in nickel, including cobalt at a 3 ppm level. However, ultimately spectrographic analysis is no better than the standards used, making these the ranking problem in nickel analysis. The status of X-ray fluoresence analysis is comparable to spectrography in both sensitivity and reliability.

In accordance with modern practice, almost all of the preferred methods for cobalt are photometric. Those which are not, are usually substantiated by a photometric determination. The basis of the great sensitivity and accuracy of photometry has been discussed earlier.

Of the methods for the analysis of nickel, those of Luke,[15] Andrew and Gentry,[8] and the ASTM[16] are recognized as authoritative. These methods were designed for determination of cobalt in electrolytic nickel in which the cobalt is present at a 0.001 to 1 per cent level. None of these methods are satisfactory for cobalt contents lower than about 0.001 per cent. The ASTM photometric method based on nitroso - R salt* is not recommended for cobalt contents below 0.01 per cent because the large amounts of reagents required tend to give high and variable blanks. A number of preconcentration approaches have been proposed to extend the nitroso - R method into the realm of trace analysis. Luke[15] separated most of the nickel by precipitation of the nickel amine perchlorate after oxidizing cobalt to the tervalent state. Steffek[17] employed a chromatographic technique to isolate cobalt. Iida and co-workers[18] utilized an

*1-nitroso-2-hydroxynaphthalene-3,6-disulfonate

ion exchange separation starting with a large sample (10 g) and again finishing with nitroso-R. Kreimer and Butylkin[19] have developed a method in which iron, cobalt and copper are extracted into chloroform as the di-antipyrylmethane adducts of the metal thiocyanates. Nickel is not extracted. The cobalt is subsequently back extracted and determined as the nitroso-R complex. Extension of the nitroso-R method by an order of magnitude to about 0.0001 per cent has been demonstrated by preconcentration.

The blue color given by cobalt thiocyanate has been known for almost a century, and has been exploited by numerous workers for the determination of cobalt. The approach has been studied systematically by Young and Hall[20] and by Uri[21] who stated that the calibration curve is nonlinear and the sensitivity too low for trace analysis. The sensitivity and selectivity of the method have been developed using a solvent extraction step to concentrate and isolate the complex thiocyanate. Various solvents have been suggested. Jackwerth and Schneider[22] have determined small amounts of cobalt in nickel by extracting $[NH_4]_2[Co(SCN)_4]$ into tributyl phosphate. If a preconcentration step is used, and if the iron content is comparable to the cobalt content, determinations in the fractional part per million range are possible.

Several large organic cations have been proposed to facilitate the separation of the cobalt thiocyanate anion from nickel. Di-antipyrylmethane in aqueous solution forms a bright-blue adduct with the cobalt thiocyanate complex. This adduct has been used for separating cobalt from large amounts of nickel both by precipitation,[23] and by extraction into chloroform.[19] In either case the final determination of

the isolated cobalt is complicated by the necessity of destroying the di-antipyrylmethane to prevent it from interfering with the reaction of cobalt with the chromogenic reagent. Babko and Danilova[24] have combined di-antipyrylmethane separation with a chemiluminesence finish[25] to determine 10^{-6} per cent cobalt in nickel. The complicated manipulations required by the chemiluminesent finish and the low reliability shown by the procedure, in addition to other restrictions imposed by the use of such a finish, severely diminishes the attractiveness of the approach.

From this review of the state of the art of determining cobalt in high purity nickel, it was apparent that a need existed for a highly reliable, simple method applicable in the part per million range. The development of such a method was undertaken with an eye toward a method which would function as a standard for other techniques.

Previous work by Flaschka and Garrett[26] on the determination of small amounts of cobalt in nickel demonstrated the potential of 1-(2-pyridylazo)-2-napthol (PAN) as a reagent for the determination of cobalt. Their work established that with PAN, cobalt could be determined in the presence of nickel, but only as long as the molar ratio of "free" (uncomplexed) nickel to cobalt did not exceed 200:1. If this ratio is not exceeded, cobalt reacted quantitatively and the cobalt(III)-PAN complex formed could be extracted into chloroform. Nickel was simultaneously extracted as the PAN complex, but could be destroyed with acid without interfering with the cobalt determination. Further details of the reactions involved in this procedure will be found in the next section.

Flaschka and Garrett were able to increase the ratio of nickel to

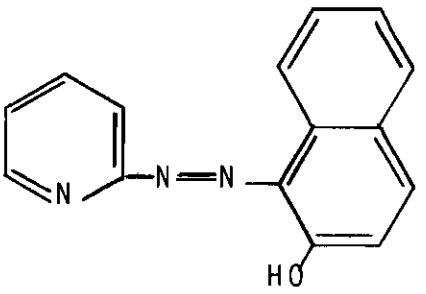
cobalt which could be tolerated in the sample by "sub-stoichiometric masking" of the nickel. The term "sub-stroichiometric masking" was used to describe a process in which the masking reagent is added to such an extent as to decrease the concentration of a foreign substance to, or below, the level at which it starts to exert an interference. In the case of cobalt in nickel, EDTA was used as the masking reagent. At pH 10 the EDTA reacts preferentially with nickel. Care must be exercised in the addition of EDTA, however, since any excess will complex cobalt, thereby blocking it from further reaction. Calculations performed by Flaschka and Garrett showed that for samples containing nickel:cobalt molar ratios in excess of 5,000:1 at least 99 per cent of the stoichiometric EDTA was needed to reduce the "free" nickel to a level at which it did not interfere. To extend the determination to higher nickel:cobalt ratios would require addition of EDTA with an accuracy even higher than the 1 part in 100 cited above. This is not feasible. This method is thus limited to the determination of about 0.005 per cent cobalt in nickel.

It was apparent that the procedure outlined above did not exhaust the full potential of the chromogenic agent involved. Better utilization would be achieved by increasing the selectivity of the cobalt-PAN reaction by means other than substoichiometric masking. A promising approach, predominantly based on kinetic phenomena, has been previously demonstrated by Flaschka and Püschel.[27] These workers showed that at pH 2 and at 0°C, nickel(II) is extremely slowly displaced from its EDTA complex by bismuth while other metal ions, including cobalt(II), react quickly under these conditions.

PAN

PAN was introduced as a sensitive chromogenic reagent for metals, and as an indicator in chelometric analysis by Cheng and Bray.[28] Since its introduction, it has been used in the determination of over thirty elements. The conditions for the reactions of PAN with numerous metal ions, including Co(III), have been studied by Püschel.[29] In addition to the determination cited above, PAN has been used by Goldstein, et al.,[30] and by Flaschka and Raheem[31] for the determination of traces of cobalt. The reagent has also been used to determine simultaneously microgram quantities of iron, cobalt, and nickel when present in comparable amounts.[32]

PAN is a red orange solid practically insoluble in water, but readily soluble in a variety of organic solvents. Nakagawa and co-workers[33] have reported a value for the distribution coefficient of PAN for a chloroform-water system of $10^{5.1}$. The structural formula for PAN is



Shibata[34] has identified three forms of PAN - a protonated form which is soluble in acidic aqueous solution, a yellow neutral form, which is water insoluble, and an ionic form present in aqueous alkaline solution. The absorbance curves of PAN in acidic and basic 1:1 chloroform:ethanol are shown in Figure 2.

PAN forms intensely colored complexes with many metals. The complexes are generally water insoluble and are readily extracted into various organic solvents. The complexes are of various shades of red except that of vanadium(V) which is deep purple, and palladium(II) and cobalt(III) which are both green.

It has been known for some time that upon addition of PAN to a cobalt solution, a red color is developed, which may convert to green. Cheng and Bray[28] attributed this to the formation of a red cobalt(II)-PAN chelate, stable in alcoholic solution, but subject to air oxidation in aqueous solution. (The stability of cobalt(II)-PAN in alcoholic solution could not be confirmed in this laboratory.) The oxidation product was said to be a green cobalt(III)-PAN chelate. Fujimoto[35] offered supporting evidence for the cobalt(III)-PAN formulation. He recorded visible absorbance spectra for both the red and green cobalt panates,* and demonstrated their stability in reducing and oxidizing media, respectively. He reported that the green panate was not formed in presence of ascorbic acid. His magnetic susceptibility measurements indicated the tervalent state for cobalt in the green panate.

Shibata[34] has recently reported the status of 2-pyridylazo com-

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*Nomenclature suggested by W. Berger, and U. H. Elvers[36]

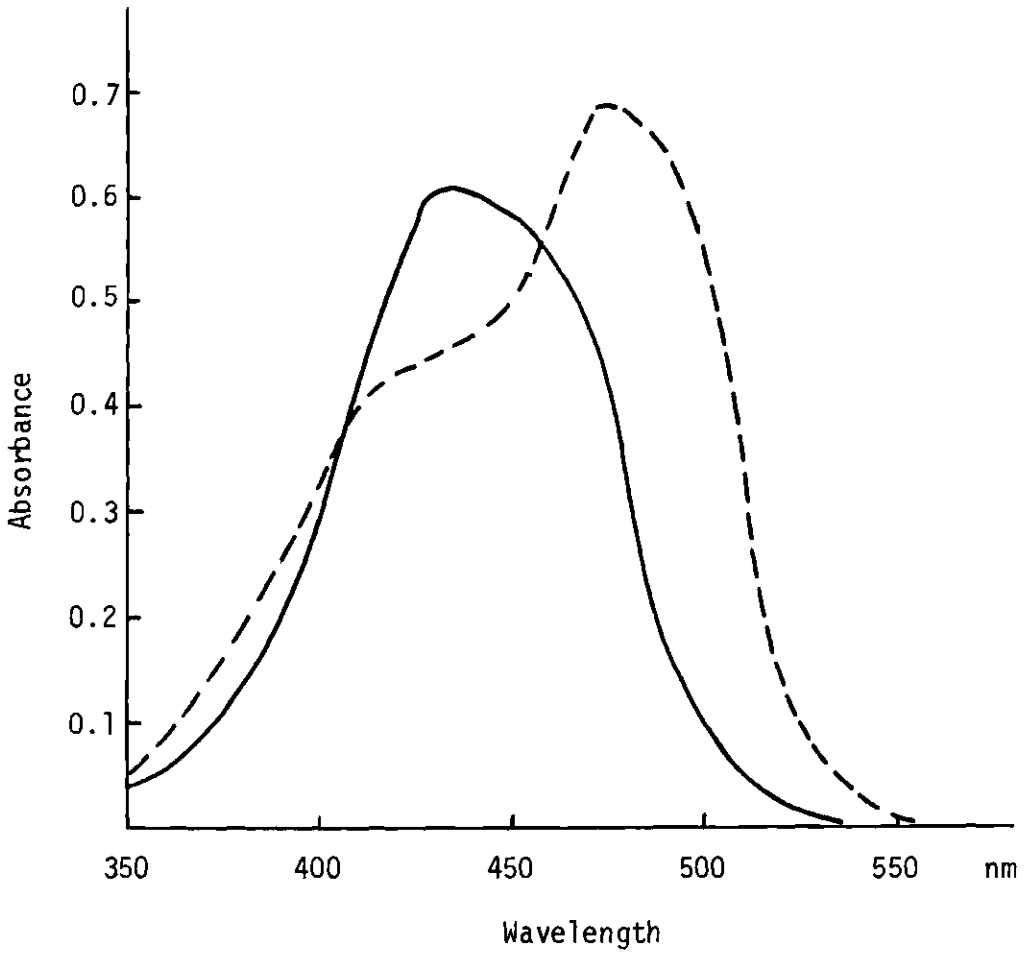

Figure 2. Spectral Curves of PAN in 1:1 Chloroform: Ethanol. Acidic ——— Basic — — —

pounds in analytical chemistry with particular emphasis on the most widely employed of these compounds, namely PAN.

Some of the characteristics of the cobalt(III) panate have been elucidated. Indications are that in solution the complex is composed of two PAN molecules per metal ion with octahedral coordination around the cobalt. Absorbance curves of the PAN complexes of some metal ions in 1:1 chloroform:ethanol, including cobalt(III), are shown in Figure 3. The molar absorptivity of the cobalt(III)-PAN complexes has been reported[32] as 2.1×10^4 liter/mole · cm. The stability constant for the complex has been reported[37] as greater than 10^{12} in 50% water dioxane. No mention is made of coblat(II) or of any experimental precaution regarding oxidation state. It is known, however, that the stability of the cobalt(III) panate is comparable to that of nickel and iron.

In addition, it has been observed that treatment of a solution of the green cobalt(III)-PAN complex with reducing agents only very slowly destroys the color. Treatment of the complex with concentrated hydrochloric acid, likewise does not immediately destroy the color as is the case with other metal panates including those of nickel and bismuth. These facts indicate that the complex is robust.

Preliminary Investigations

It was concluded from the data outlined in the preceding sections that a practical method for determining cobalt in nickel could be developed. The method would take advantage of the high sensitivity of PAN as a chromogenic agent for cobalt(III), the selectivity afforded by the characteristic green color of the cobalt(III)-PAN complex, the efficient

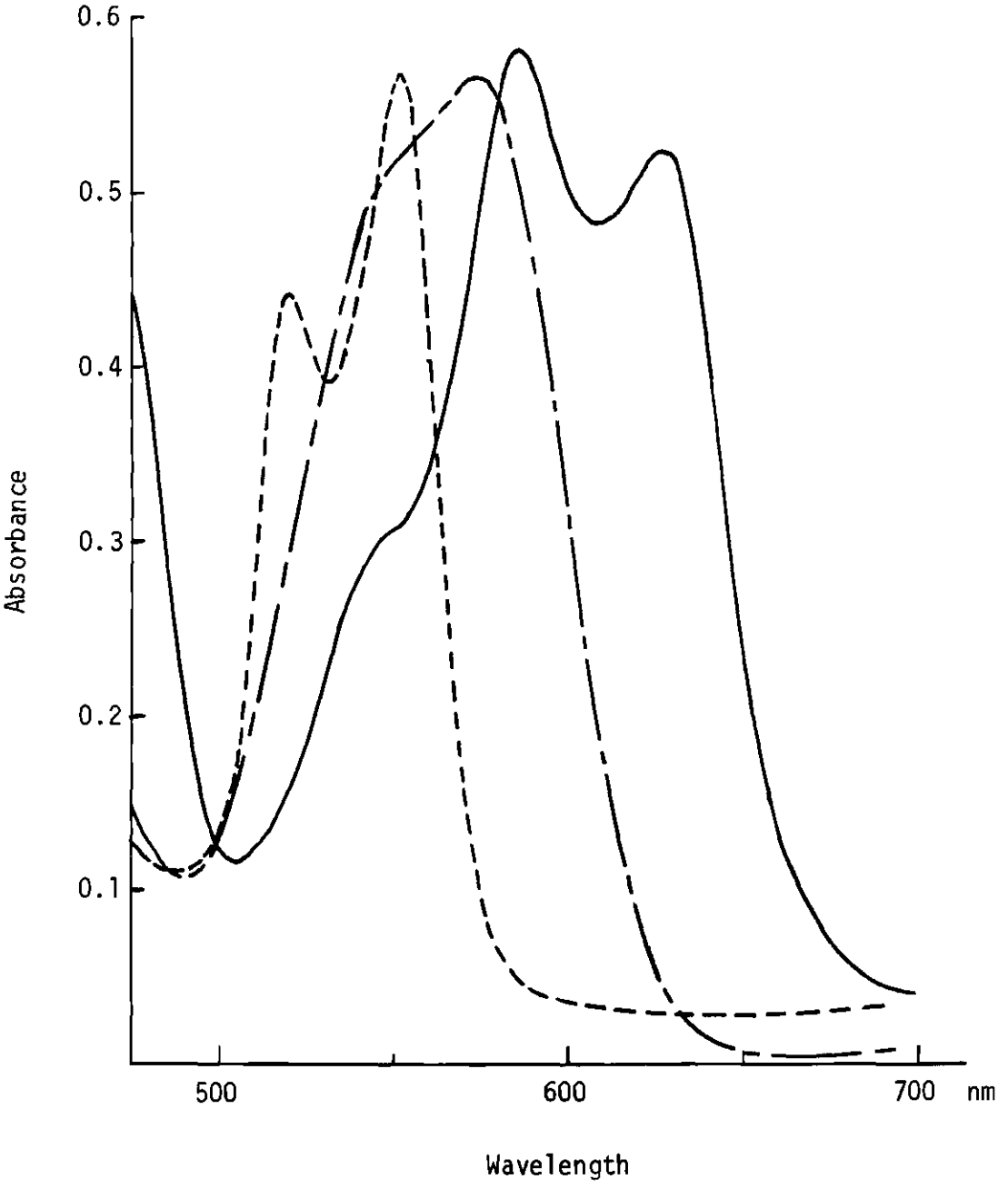

Figure 3. Spectral Curves of Some Metal Complexes of PAN.
Cobalt(III) ——— Bismuth(III) —— – ——
Nickel(II) — — —

masking of nickel by EDTA, and the robust nature of both the nickel-EDTA and the cobalt(III)-PAN complexes. The procedure would involve the initial titration of both cobalt and nickel with EDTA, after which the cobalt would be selectively displaced by bismuth. The now uncomplexed cobalt would be reacted to form the cobalt(III) panate. This panate would be extracted to separate it from the nickel and the absorbance of the cobalt(III) panate in the extract would be measured. The development of a practical procedure is described below.

As a first step, studies were conducted to find the rate of formation of the cobalt(III)-PAN complex. For these studies the total immersion photometer described in Chapter V was used. The use of this instrument allowed the absorbance of cooled solutions to be recorded as a function of time. To perform such photometric studies with a common photometer would be quite difficult. Discussion of the instrumental aspects of this investigation will be found in Chapter V.

The formation of the cobalt panate was monitored by recording the transmittance of the test solution at 625 nanometer (nm). No simple rate expression could be deduced from the data. The temperature dependence was as expected - a decrease in temperature leading to a greatly reduced rate of reaction. At 0°C the formation of cobalt(III)-PAN from Co(II) and PAN was found to be essentially complete after twenty minutes in 50 per cent ethanol, while at room temperature only about five minutes was required. The presence of either nickel(II) or nickel-EDTA was found to reduce the rate of cobalt panate formation, and uncomplexed nickel(II) or EDTA reduced the maximum absorbance when the total of uncomplexed metals (cobalt plus nickel) exceeded the amount of PAN added.

The identity of the oxidizing agent involved in the conversion of cobalt(II) to cobalt(III) remains obscure. No noticable change in the rate of formation of Co(III)-PAN was observed when oxygen was excluded or when periodate, peroxide, or elemental bromine was added. It is the suspicion of the author that PAN itself is involved in the oxidation.

In order that the masking of nickel by EDTA be effective without interfering with the formation of the cobalt(III) panate, it is necessary that a small controlled excess of EDTA be added. To accomplish this, nickel is converted to the EDTA complex by titration. The titration is performed at pH 10 using murexide as indicator.[38] The sluggishness of the reaction between nickel and EDTA requires that the solution be warmed (50-60°C). Under these conditions murexide undergoes rather rapid decomposition so it was added just prior to the end point. It was established that neither murexide nor any of its decomposition products interfered in later stages of the procedure.

In order that solution volume not becomes excessive, it was desirable that the EDTA titration be performed with rather concentrated solutions. The moderate solubility of EDTA precluded use of a highly concentrated solution; therefore, most of the EDTA was added as the solid di-sodium salt. The titration was then completed with 0.15 F EDTA.

After addition of buffer, the sample solution was about 0.5 F in nickel. The deep color of this solution and of the nickel EDTA solution past the equivalence point, made end point detection difficult. The difficulty is not so serious as might be imagined however, since an accuracy of only a few per cent is required. Against the deeply colored background of the concentrated solution, the color change was seen as a rather

sharp change from dark, dirty green to clear, deep violet. The murexide was added as a 2 per cent solid mixture with sucrose or sodium chloride.

Since kinetic masking of nickel was demonstrated by Flaschka and Puschel[27] at 0°C, it was initially decided to use temperatures near 0°C for the analytical procedure. Subsequent investigations have shown that in 50 per cent ethanol the demasking of nickel by bismuth is so slow that cooling is not required, and operation at room temperature is possible.

However, it was found that in alcoholic solution even at room temperature the displacment of cobalt from its EDTA complex is also slow. Rate studies have indicated that the presence of alcohol reduces the effectiveness of the bismuth in displacing other metals from their EDTA complexes. On addition of ethanol to the sample solution containing bismuth, turbidity was seen to develop, followed by the appearance of a white precipitate. It is likely that this is due to interaction of the bismuth and ethanol in a solvolysis reaction. This would account for the slowness of displacement in alcoholic solution. Unfortunately, the use of ethanolic solutions cannot be avoided because the metal panates and PAN itself are only very slightly water soluble. The problem of reduced activity for bismuth was resolved by addition of bismuth to the solution containing the metal EDTA complexes before the addition of alcohol. The precipitation of excess bismuth was avoided by the addition of tartaric acid.

Having established that cobalt could be selectively converted to the PAN complex; it was next necessary to find the conditions for the separation of this complex from large amounts of nickel EDTA. This problem was previously handled by Flaschka and Garrett[26] by a chloroform ex-

traction. It was pointed out by these authors that for effective extraction a low percentage of alcohol in the solution is essential. To help in understanding the effects of solvent composition throughout the determination, a phase diagram of the water-ethanol-chloroform system was constructed from experimental data gathered for the purpose. The diagram is shown in Figure 4. Two important deductions were made from the phase diagram. First, it was seen that a one phase system would result for solutions with an overall ethanol content greater than 37 per cent. Second, the diagram revealed that the water content of the organic layer is reduced as the per cent ethanol in the system is reduced. For reasons discussed later, low water content in the extract is desirable. It is advantageous, therefore, to add a large quantity of water to the alcoholic sample solution prior to extraction.

Published data[30] on the extraction of the cobalt(III) panate indicated that extraction could advantageously be conducted over the range from pH 4 to 7. No data was available on extractions below pH 4 and therefore relevant studies were conducted. The results show that the recovery of cobalt is quantitative with three extractions from solutions in which the hydrogen ion concentration is from 0.1 M to 0.5 M. Nickel EDTA is not extracted. These acidic conditions have the added advantage of improving phase separation.

At this point a workable procedure was achieved which is schematically shown in Figure 5. This diagram shows the major steps in the procedure with EDTA indicated by the symbol Y, and with charges largely omitted. Only major species present at each step have been included.

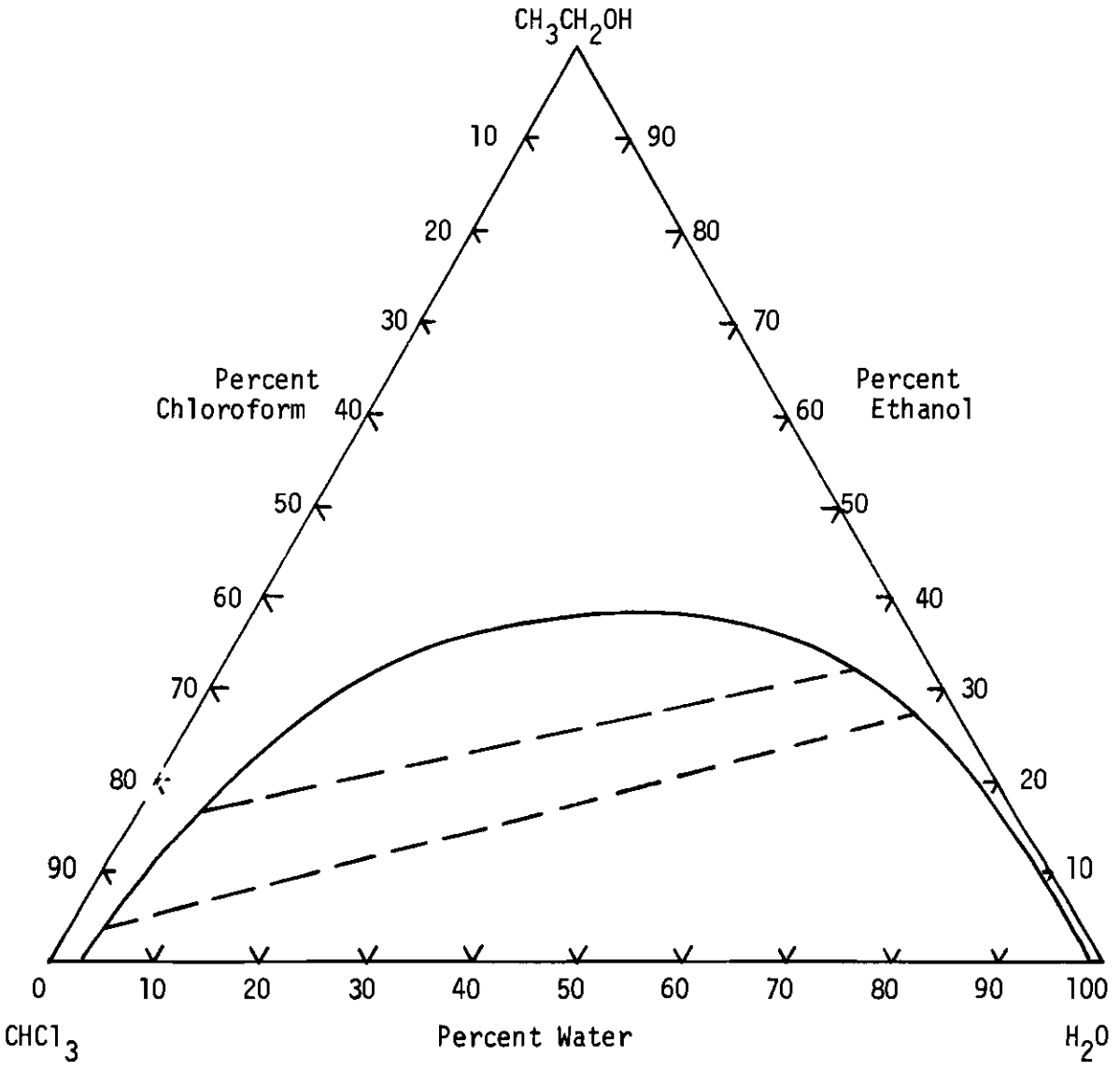

Figure 4. Phase Diagram for the Chloroform:Ethanol:Water System Including Tie Lines.

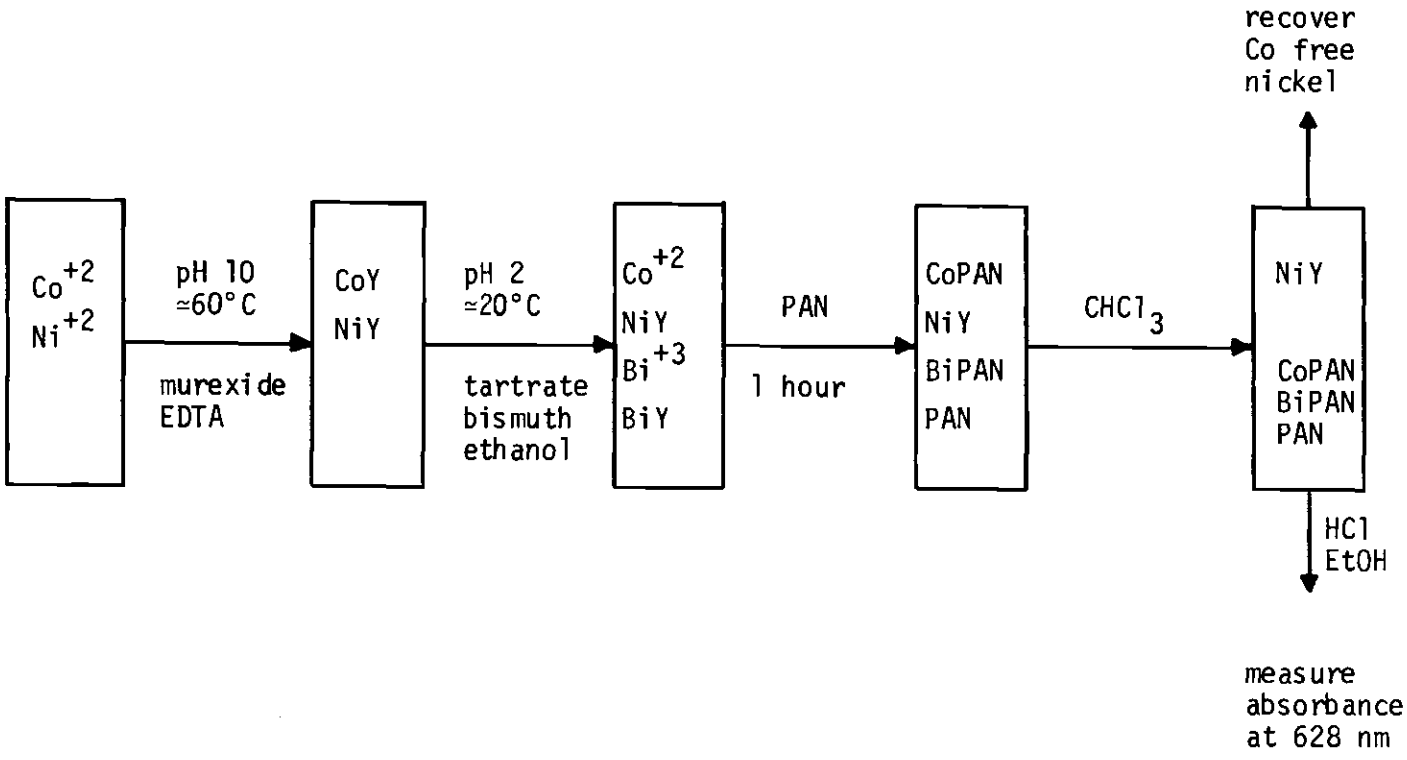

Figure 5. Schematic Diagram of the Procedure for Analysis of Cobalt in Nickel.

Development

Several aspects of the procedure outlined in Figure 5 were studied to achieve optimum conditions for cobalt determination. The first of these was the ruggedness of the Co(III)-PAN formation with regards to the presence of free (uncomplexed) bismuth, EDTA, and tartrate. The results indicated, as expected, that large excesses of bismuth are to be avoided. Quantitative recovery of cobalt resulted as long as the bismuth excess was not sufficient to cause precipitation, which occurred when the bismuth concentration exceeded approximately 10^{-3} M. The presence of tartrate was shown to be useful in preventing precipitation and thereby the interference. A portion of the excess bismuth was seen to form a red panate under the conditions chosen. This species was entirely destroyed by acidification of the extract.

No "free" EDTA could be tolerated. It was found that sufficient EDTA was required to completely complex all nickel and other metal forming complexes at pH 2. An excess of EDTA over this requirement was found acceptable so long as the excess did not exceed the amount of bismuth subsequently added to displace cobalt. After the cobalt(III) panate was formed, an excess of EDTA did not interfere with the analysis. Very large amounts (2 gm) of tartaric acid were found to lead to low results.

Since the masking of nickel by EDTA relies on kinetic phenomena, considerable study was devoted to time relations in the procedure. At two points in the procedure some consideration must be given to time. First, after the metal sum has been titrated with EDTA, bismuth is added to displace metals other than nickel. The excess free bismuth must not be allowed to act for long periods on the nickel-EDTA solution, because

the displacement of nickel proceeds, though slowly. As discussed below, small amounts of released nickel offer no serious complication, but larger amounts lead to complications. Deactivation of the bismuth was achieved by the addition of ethanol. Time studies show that this addition should be done within a half minute of the introduction of bismuth at 20°C and within three minutes at 10°C. Low results were encountered if these times were extended.

The second point in the procedure where time was an important factor is the time required for the formation of cobalt(III)-PAN. Under all practical conditions a waiting period of one hour was found sufficient for complete formation of the cobalt(III)- panate.

A study was also conducted to establish the effect of solvent composition on the absorptivity of the cobalt(III) panate. Two solutions containing identical concentrations of cobalt(III) panate, one in chloroform and one in ethanol, were prepared. There was no detectable difference in their absorbance at 625 nm. When these solutions were mixed in various proportions and the absorbance of the mixtures measured at 625 nm, the absorbance was found to vary only slightly with solvent composition. Over the region of solvent compositions anticipated in practical analysis, no observable variation seemed likely. Puschel[29,32] has demonstrated that the absorptivity of the cobalt(III) panate does not vary with pH over the range from pH 4 to pH 11.

When solutions containing cobalt-EDTA and nickel-EDTA were treated with bismuth and PAN, the spectrum of a chloroform extract showed a small shoulder at 560 nm. The shoulder was found to be due to the absorbance of the bismuth PAN complex and the nickel PAN formed from a small amount

of the nickel displaced from its EDTA complex by bismuth. The tail of the absorbance peaks of these species was of low but measurable magnitude at the wavelength chosen for the determination of cobalt, 625 nm. The problem could be obviated by the addition of a few milliliters of concentrated hydrochloric acid to the extract in order to destroy both of these complexes. The cobalt(III) panate, however, is inert towards the acid for several hours.

Two minor complications arose with the addition of acid to the extract. First, a red color became apparent in the chloroform solution of PAN employed as the blank. This color is apparently due to the presence of a protonated form of PAN. The effect of this phenomenon was found to be negligible as long as the blank and the sample were treated identically.

Second, the addition of acid causes the appearance of an aqueous phase. This problem was overcome by using ethanol for dilution to volume prior to absorbance measurement. At this point the desirability for low water content of the extract becomes apparent. A large quantity of water in the extract, combined with that introduced by the addition of acid would dictate a large volume of ethanol to produce a single phase. The dilution would decrease absorbance and therefore lower the sensitivity.

It was apparent that the lower limit on the determination of cobalt is fixed by the minimum quantity of cobalt which will allow quantitative determination in the final extract. This minimum quantity is in turn a function of the final extract volume since the limit of quantitative determination is concentration dependent. It was therefore of interest to investigate the possibility of reducing the volume of the final extract,

thereby extending the effective sensitivity of the method. An alternate approach, increasing effective sensitivity by increasing sample size, was not pursued. Large samples are undesirable from a practical standpoint because of the high cost, and because of the problems associated with the large volumes of solutions which result.

The feasibility of volume reduction was demonstrated by experiments in which the normal 50 ml volume of the final extract was reduced to 25 ml. This reduction was accomplished by stripping off a portion of the extraction solvent. For this purpose specially constructed 25 ml volumetric flasks with 25 ml bulbs in the flask neck were used. The cobalt (III) PAN extract was placed directly in the flask and the solvent partially removed by heating in a warm air bath. A Teflon ring hanging by a glass fiber was inserted in the flask to serve as a "boiling stone." When the solvent stripping was accomplished before addition of concentrated HCl at the final step of the procedure, quantitative retention of the cobalt(III) PAN absorbance was observed. A comparable increase in effective sensitivity without loss of precision would be possible utilizing a 2 cm pathlength cell. A combination of these approaches could be used to further increase sensitivity. Data from determinations utilizing post concentration by solvent evaporation are included in Table 2.

Experimental

Procedure

1. Dissolve sufficient sample to contain from 2 to 100 µg of cobalt in 1:1 nitric acid (Note a).

2. Add aqueous ammonia until all the nickel has been converted

to the deep blue nickel amine complex, then add 10-15 ml of Buffer pH 10.

3. Add approximately 95 per cent of the stoichiometrically required quantity of solid di-sodium EDTA (Note b). Heat the solution and add water until all the solid EDTA is dissolved. The total volume should not exceed 100 ml.

4. To the hot solution add a spatula tip of murexide indicator (Note c) and titrate with 0.15 F EDTA until a permanent violet end point is reached. Add 1 ml excess EDTA.

5. Add about one gram tartaric acid and allow the solution to cool to room temperature.

6. Adjust the "pH" (Note d) to about 2.5 (Note e).

7. Add 2 ml of 0.1 F bismuth nitrate and adjust the "pH" to a value between 1.8 and 2.0.

8. Add sufficient ethanol to yield a 50 per cent mixture and re-adjust the "pH" to a value of 2.0.

9. Add 2 ml of 0.01 F PAN and allow one hour standing time.

10. Estimate the volume of the test solution, and add an equal volume of water to a separatory funnel followed by 10 ml of 2 F HCl per 100 ml of test solution. Add the test solution to the funnel.

11. Extract the sample solution with four, 5 ml portions of chloroform combining the extracts in a 50 ml volumetric flask (Note f).

12. Add 2 ml of concentrated HCl and dilute to the mark with 95 per cent ethanol.

13. Measure the absorbance of the test solution at 625 nm using as reference a blank prepared as above, but without sample addition (Note g).

Notes

a. About 20 ml of 1:1 nitric acid will be required for each gram of metallic nickel dissolved.

b. The stoichiometric requirement is 6.34 grams of $Na_2H_2Y \cdot 2\ H_2O$ per gram of nickel.

c. The murexide indicator is added as a finely ground mixture of 2 per cent murexide in sucrose.

d. The concept of pH as defined in aqueous solution is not intended. Rather the term "pH" is used to indicate the reading of the Beckman Zeromatic II obtained when a glass electrode and a calomel electrode are used with the meter and are immersed in the alcoholic test solution.

e. Most masking reagents should be added at this point. Add 1 ml of 85 per cent phosphoric acid to mask iron. Add 1 to 3 ml of a saturated aqueous solution of thiourea to mask more than 0.2 per cent copper(II) or any palladium(II).

f. The solution may be stored for at least 24 hours without deterioration at this point in the procedure. Also at this point the volume may be reduced by evaporation if desired.

g. After addition of acid the absorbance of the solution should be measured within one hour.

Calibration Curve

Prepare a calibration curve by following the above procedure from step two for solutions containing known quantities of cobalt nitrate. The cobalt content of these standard solutions should be from 10 to 100 µgm in about 50 ml.

Discussion

Results

A calibration curve was prepared according to the procedure and is presented in Figure 6. The plot shows a linear relationship between absorbance and concentration from 0 to 2.0 μgm cobalt per milliliter. The molar absorptivity calculated from the slope of the calibration curve is 2.1×10^4 liter/mole-cm. This value is identical with that reported by Püschel, et al.[32] (Note that the absorbance values for the calibration curve shown were determined with a cylindrical cell with an effective pathlength of 11.7 mm). The Sandell sensitivity[2] is 0.0029 $\mu gm/cm^2$.

Table 1 presents the results obtained for the determination of cobalt when present alone. The data show a satisfactory accuracy and precision. It should be recognized that a variation of absorbance by 0.008 units corresponds to 1 μgm of cobalt.

Evaluation of the influence of nickel was initially assessed by addition of nickel to solutions containing known amounts of cobalt and then analyzing for cobalt. The results were, as expected, high due to the presence of small amounts of cobalt impurity in the nickel. Once adjustment for this factor had been made, nickel, even when present in very large amounts, had no effect on the accuracy of the method.

A sample of "cobalt-free" nickel was prepared for use in the preparation of synthetic samples of lower cobalt content than that of the high purity nickel available, and for use in experiments designed to further test the validity of the method in the presence of nickel. The preparation of this nickel was accomplished by a procedure parallel to the analytical procedure here described. A sample of high purity nickel

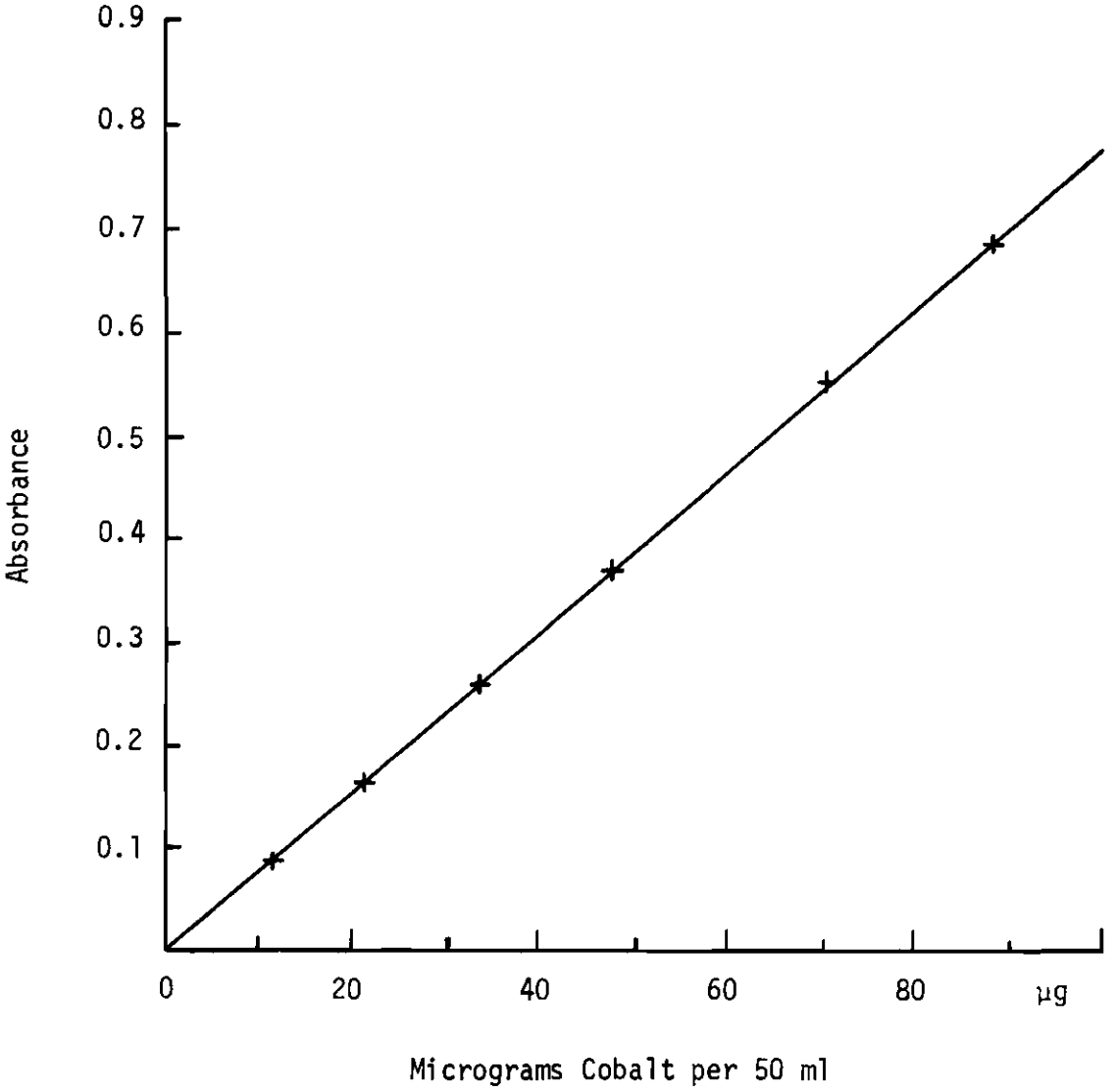

Figure 6. Cobalt Calibration Curve.

Table 1. Analysis of Cobalt

µgm Co taken	µgm Co found	Δ
11.0	10.8	-0.2
11.0	10.8	-0.2
11.6	11.6	0.0
11.6	11.6	0.0
14.5	14.7	+0.2
22.0	21.7	-0.3
22.0	21.4	-0.6
22.0	22.7	+0.7
23.2	23.0	-0.2
23.2	23.3	+0.1
28.9	29.1	+0.2
33.0	32.9	-0.1
33.0	31.9	-1.1
33.0	33.1	+0.1
34.8	35.2	+0.4
34.8	35.4	+0.6
55.0	56.6	+1.6
55.0	55.0	0.0
66.0	66.1	+0.1
99.0	101.9	+2.9

was carried through the analytical procedure to the point of extraction (Step 11). The extract containing the cobalt was discarded, and the aqueous solution was concentrated by evaporation. The first solid to separate from the concentrated solution was crystalline ammonium chloride. On further evaporation, nickel EDTA crystals began to appear. At this point the mother liquor was decanted and blue crystals of nickel EDTA collected. These crystals were redissolved and recrystallized several times. The EDTA was then destroyed by heating to fumes in concentrated sulfuric acid, and the metallic nickel recovered by electrodeposition from ammonium tartrate solution under the conditions specified by Torrance.[39] No traces of cobalt could be detected in either the nickel-EDTA or the metallic nickel. A portion of the recrystallized nickel-EDTA was analyzed for nickel content and used directly in the preparation of synthetic samples of low cobalt content. The synthetic samples were analyzed and the results are shown in Table 2. Analysis of sub part per million range cobalt was accomplished with such synthetic samples.

Two approaches were found useful in evaluating the cobalt content of high purity materials. The first of these is the standard addition technique. In the standard addition method, absorbance is determined for two solutions; one containing an aliquot of the unknown, the second containing an identical aliquot of the unknown plus a precisely known volume of a standard solution of the element being determined. Normally, a series of standard additions are made and the resulting absorbances are plotted against the amount of the standard increments. The graphic presentation of the standard addition evaluation of cobalt in a 0.950 gram sample of J. T. Baker Reagent nickel shot is shown in Figure 7. The cobalt found

Table 2. Representative Results of Analysis of Synthetic Nickel Samples

μg Co		gm/Ni	ppm Co	
taken	found		taken	found
0.7	0.9	0.82	0.8	1.1
1.4	1.5	0.93	1.5	1.6
5.3	5.6	2.34	2.4	2.3
5.3	5.1	1.65	3.1	3.0
1.4	1.5	0.40	3.5	3.7
2.7	2.7	0.64	4.2	4.2
5.3	4.6	1.12	4.1	4.7
5.3	4.9	0.95	5.1	5.6
2.7	2.6	0.48	5.4	5.6
1.4	1.4	0.25	5.6	5.6
2.7	2.8	0.48	5.8	5.6
4.0	4.0	0.71	5.6	5.6
32.8	33.0	0.71	46.2	46.5

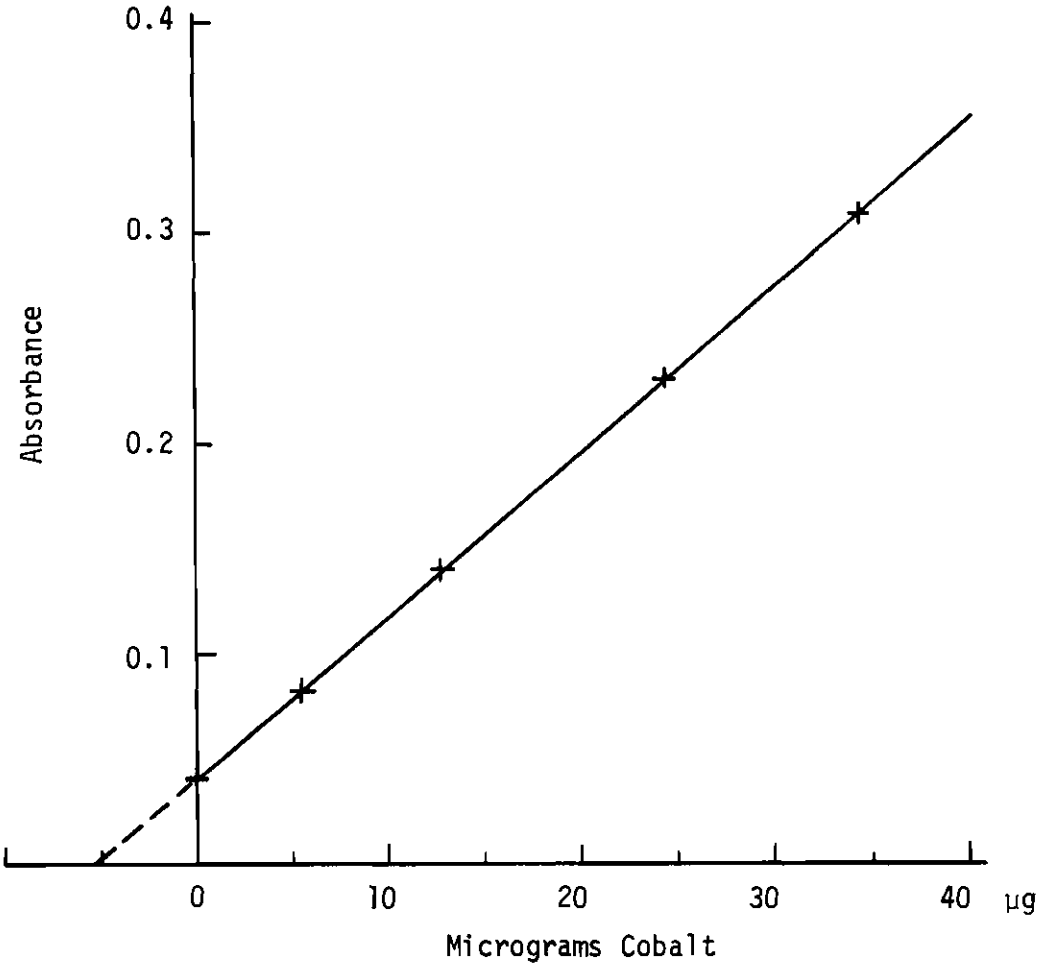

Figure 7. Evaluation of Cobalt in Nickel by Standard Addition.

corresponds to 5.4 parts per million.

The second technique utilized for evaluation of the cobalt content of the nickel was direct analysis. Table 3 presents the results of the direct analysis of the J. T. Baker nickel shot. The cobalt content of the nickel was found to be 5.4 ± 0.2 parts per million. The agreement between the two techniques was satisfactory.

Interferences

One of the most attractive features of the method here described for the determination of cobalt is its insensitivity to the presence of foreign ions. The results of extensive work on the elimination of potential interferences is summarized below. For many elements the study has been extended to impurity levels far above those expected in high purity nickel. This has been done to provide a basis for the evaluation of the potential of the method for application to nickel samples of lower purity, and to alloys and salts.

Only a very few metals are able to react with PAN under the conditions for formation of the cobalt panate. The panates of most of these metals are stable only above pH 2 and are readily destroyed in the acidification (Step 12). Cobalt(III)-PAN is a notable exception. An indication of the relative stabilities of some metal panates and their dependence on "pH" is shown in Figure 8. The curves of Figure 8 show the degree of formation of various metal panates (as a percentage of maximum absorbance) as a function of pH. These curves were recorded at a wavelength near the absorbance maximum for each metal panate, in 50 per cent ethanol, aqueous solution.

Table 3. Results of Analysis of Standard Nickel

mg Ni taken	µg Co found	ppm Co
476	2.7	5.6
952	5.3	5.6
476	2.5	5.3
952	4.9	5.2
714	3.8	5.3
831	4.2	5.1
1070	5.9	5.5
475	2.5	5.3
950	5.1	5.4
1425	7.6	5.3
	Avg.	5.36
	Std. dev. =	0.1_6

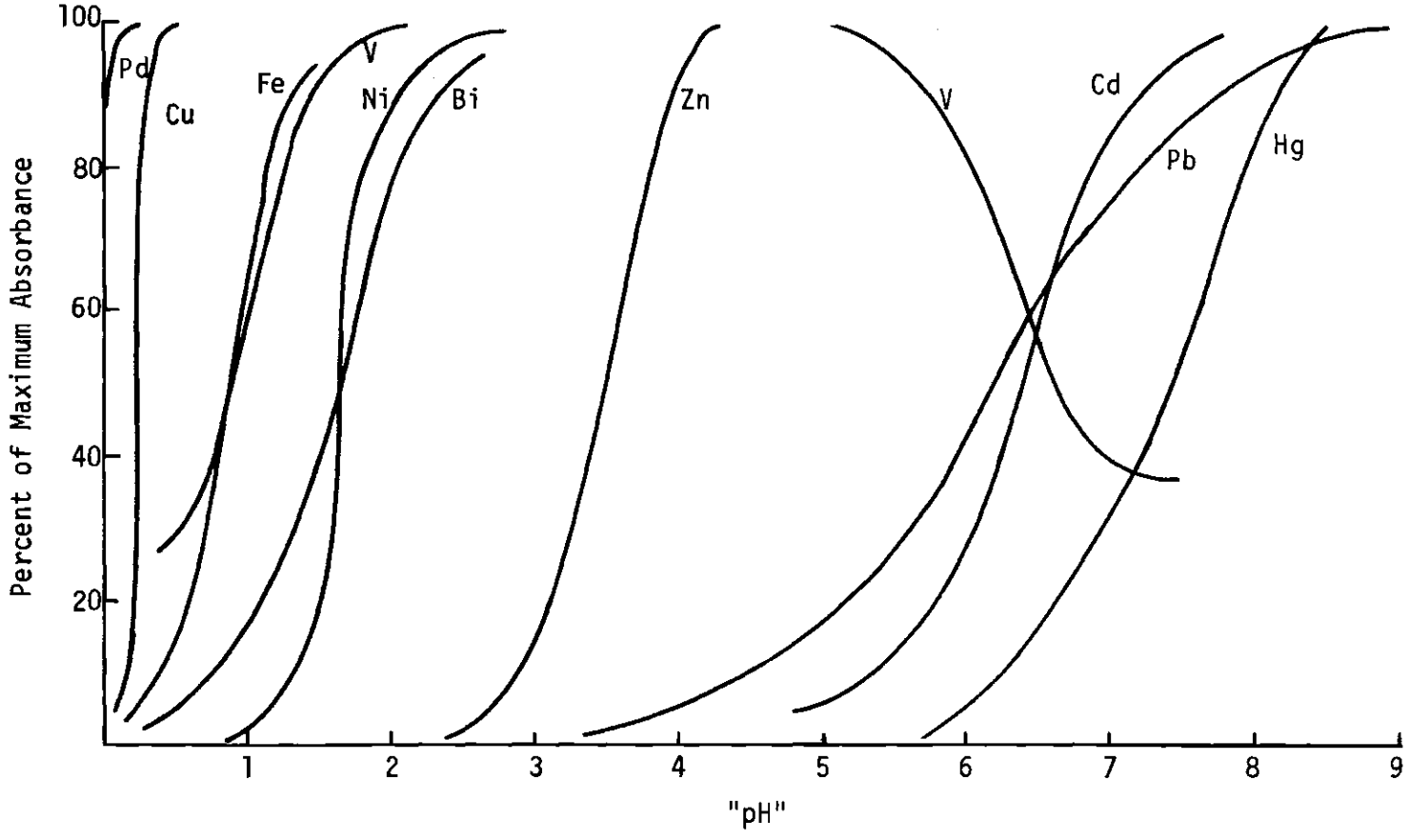

Figure 8. Degree of Formation of Various Panates as a Function of "pH"

The metallic elements fall into three groups with reference to their potential to interfere with the cobalt determination. Group I contains those metals which have not been reported or observed to form panates. These are the alkali metals, the alkaline earth metals, Cr, Mo, W, Tc, Re, and the actinides excluding Th and U. These elements do not directly interfere with the cobalt determination and in general are of little concern. Indirect interferences are possible, as for example, barium does not compete directly with cobalt for PAN, but in the presence of sulfate, barium sulfate will precipitate and may interfere by absorption or occlusion.

Group II contains those elements which form PAN complexes of such high stability that they are formed at pH 2 and may thus interfere with the cobalt-PAN reaction. These elements are evident from Figure 8. They are copper(II), bismuth(III), vanadium(V), iron(III), palladium(II), and nickel(II). The action required to handle these elements and their potential to interfere is discussed below.

Group III includes the remainder of the metals. This large group contains those metals which form PAN complexes of low stability. For these elements the minimum pH for complex formation is higher than 2. Some of these elements are included in Figure 8. When present in the amounts expected in the analysis of high purity nickel, elements of Group III do not interfere. If present in very large amounts, these elements may interfere by complexing with PAN; for in this case the fraction of metal so complexed may be very low, but the quantity complexed may be large enough to tie up the available PAN.

The potential interference of Group II metals has been studied in some detail. No interference occurs as long as there is sufficient PAN available to react with all of the cobalt. This situation will exist when the total equivalents of the metals from Group II, not complexed with EDTA, is less than the number of equivalents of PAN available. Under these conditions cobalt will be entirely converted to the panate. Subsequent extraction and acidification will destroy panates other than those of cobalt(III) and palladium(II).

At higher total impurity levels the free metal content may exceed the available PAN resulting in incomplete conversion of the cobalt to its panate. Increased amounts of PAN will diminish the loss, but this approach should be reserved for cases not amenable to other techniques, because high blanks are encountered. In cases of high metal content, masking in general offers a more satisfactory approach. The upper limit of tolerance for metals of the last group, without modification of the basic procedure, was not precisely determined, but in no case was the limit lower than 0.1 per cent based on nickel.* These limits are well above the impurity levels encountered in analysis of high purity nickel. Some representative results are shown in Table 4.

Specific masking techniques have been developed for the metals in the last group, which contains the metals forming very stable panates. Nickel is masked as the EDTA complex as previously discussed. No practical limit could be found for the masking of nickel with EDTA.

*Specification of impurity levels in terms of a percentage based on nickel has been used to correspond to practice in specification of the purity of metal samples. The more glamerous, but less meaningful, expression of impurity level as a ratio to determined element has been avoided.

Table 4. Representative Results of Analysis of Cobalt in Presence of Foreign Ions

Cobalt µg			Foreign Ion	
Taken	Found	Difference	Symbol	Level
32.8	33.0	+0.2	Zn	0.09%
30.9	31.5	+0.6	Zn	0.36%
25.7	25.5	-0.2	Mn	0.05%
25.7	25.3	-0.4	Pb	0.18%
25.7	25.3	-0.4	Pb	0.22%
25.7	24.7	-1.0	Pb	0.54%
25.7	25.3	-0.4	Pb	0.66%
25.7	25.0	-0.7	In	0.97%
25.7	25.3	-0.4	Tl	1.70%
37.3	32.9	+0.2	Cu	0.13%
37.3	37.9	+0.2	Cu	0.27%
37.3	36.2	-1.1	Cu	1.3 %*
25.7	25.3	-0.4	Cu	0.27%
23.2	23.1	-0.1	Pd	0.04%
25.7	24.8	+0.9	Pd	0.45%
25.7	25.3	-0.4	V	0.02%
25.7	24.1	-1.6	V	0.02%
37.3	37.5	+0.2	Fe	0.35%†
53.9	53.0	-0.9	Fe	0.05%†
25.0	26.0	+1.0	Fe	0.33%†
25.7	24.2	-1.5	Sn(IV)	0.12%
25.7	24.6	-1.1	Sn(IV)	0.12%
25.7	22.0	-3.7	Sn(IV)	0.50%
25.7	26.5	-0.8	Sn(II)	0.99%††

*Thiourea masking

†Phosphate masking

††Addition PAN required

At the point of PAN addition, Step 9, bismuth is effectively masked as either the tartrate or EDTA complex. Only if an excess is added at Step 7 will there be the possibility of sufficient free bismuth to cause interference. Bismuth in the sample is without effect.

Iron(III) is conveniently masked with phosphate or pyrophosphate. The masking reagent is added during the acidification prior to bismuth addition. Then, when iron is displaced from the EDTA complex by bismuth addition, it is bound in the phosphate complex and prevented from reacting with PAN. Pyrophosphate has been successfully employed to mask iron, but has the disadvantage of impeding the extraction of cobalt(III)-PAN necessitating extraction with an additional portion of chloroform to insure complete recovery of cobalt. For this reason phosphate was added as phosphoric acid at Step 6. At least 0.3 per cent iron in nickel can be masked in this manner.

The masking of vanadium with hydrogen peroxide has been suggested by Püschel et al.[40] The technique involves formation of the peroxovanadate complex. The formation of this complex at pH 2 is insufficient to prevent vanadium from reacting with PAN, and high results are obtained for cobalt. (The absorbance maximum for VO_2^+-PAN is at 615 nm). However, small quantities of vanadium, up to about 0.02 per cent (in the nickel), can be effectively destroyed by acidification, of the extract. Larger amounts may be masked by peroxide if the procedure is modified at Step 8 so that Co(III)-PAN is formed at pH 3.5 or higher. However, at this pH the formation of the cobalt panate is even slower and the number of potential interferences is significantly greater. For these reasons per-

oxide masking can not be recommended. The restriction of low vanadium content is not serious for analysis of high purity nickel.

Up to about 0.25 per cent copper can be handled by acidification after the extraction. This limit is several orders of magnitude greater than the highest level for copper expected in high purity nickel. However, the allowable copper content can be further extended by masking the copper with thiourea which is added at Step 6 just prior to the bismuth (Step 7).

Thiourea has also been utilized to mask palladium(II). Masking of this metal is necessary under any circumstances since it withstands the acid treatment and has its maximum absorbance at about 678 nm, which is quite close to the operating wavelength. At least 0.5 per cent palladium can be masked by addition of 1 to 3 ml of a saturated aqueous solution of thiourea just prior to the addition of PAN. Representative results of analyses performed in the presence of interfering ions discussed are given in Table 4.

An additional group of possible interferences studied were those materials that could interfere by a mechanism other than competition for PAN. Some reducing agents, such as $S_2O_3^{=}$, and Sn^{2+}, were found to interfere. Mild reducing agents prevent the oxidation of cobalt to the tervalent state. Stronger reducing agents destroy the PAN. In either case, the interference can be eliminated by boiling the sample solution with nitric acid before starting the procedure. Care must be taken to avoid high concentrations of species which might precipitate in the 50 per cent alcoholic solution, since the presence of precipitates leads to low re-

sults for cobalt. Large excesses of PAN produced high blanks leading to loss of precision. Elemental halogens interfere by destroying PAN. Other species likely to be present in the solution, including chloride, nitrate, and sulphate did not interfere even when present in abnormally high concentrations.

One interference remains unresolved. The presence of Sn(IV) causes low results. The mechanism is not clear. Shibata[34] reports a red Sn(IV) panate, but this has not been confirmed. Indications are that the tin(IV) interferes not with the formation of cobalt(III)-PAN, but rather with the extraction process. Further investigation of this phenomenon has not been conducted since at a tin content of 0.1 per cent which is very high for high purity nickel, the error due to the tin is less than 3 per cent relative in the cobalt value.

Conclusions

The method here developed has been demonstrated to be highly accurate and reliable for the determination of cobalt in high purity nickel. The method is highly sensitive, allowing determination of part per million range cobalt in nickel directly and sub-part per million range cobalt if a concentration step is included. This represents at least an order of magnitude improvement over the best photometric techniques described earlier. Only the chemiluminesence technique of Babko and Danilova[24] claims a lower detection limit. The low reliability of this approach has been mentioned earlier.

Trace analysis is normally characterized by fastidious concern for the details of cleanliness of apparatus and purity of reagents. Per-

haps the most attractive feature of the cobalt analysis as described, is its insensitivity to the presence of foreign substances, and the corresponding simplification of the procedures used.

The method outlined here shows promise for application in three areas. First, it offers a straightforward, reliable method for analysis of standards prepared for calibration of an emission spectrograph. Emission spectrography remains the method of choice for routine analysis of part per million range cobalt, in nickel samples of nearly invarient matrix composition. Second, the method provides a technique for the determination of low level cobalt without the need for complex or expensive instrumentation. Third, it offers a method suitable for analysis of cobalt in nickel samples of varying composition.

CHAPTER V

DESIGN AND CONSTRUCTION OF A FULL-IMMERSION PHOTOMETER

Introduction

Although the development of photometric titrations spans a period of 50 years, the methods are still not fully appreciated. Two reasons for this situation have been mentioned by Flaschka.[47] First, the theoretical basis of photometric titrations is frequently not sufficiently appreciated, so that important applications are overlooked. Second, the development of adequate instrumentation has been slow. It is this latter point which is of prime concern here.

Throughout the development of photometric titrations, commercial photometers have been used in the majority of cases to conduct the titration.[41] The conversion of most commercial photometers for use as a titrator, especially one destined for use in routine analysis, requires some drastic changes, and the resulting instrument is seldom adequate as a general-purpose phototitrator. For this reason, many workers have chosen to construct their own instruments. A few of these will be mentioned below, following a brief description of the characteristics desired in an ideal phototitrator and the relation of such an instrument to a photometer.

The desiderata of an ideal titrator have been delineated,[47] and the main points are the following. (i) The ability to work without exclusion of ambient light; thus allowing observations to be made during

the titration and eliminating many restrictions on cell configuration. (ii) The possibility of expanding the scale above the 100 per cent T point in order to increase sensitivity, thus allowing titration of systems involving only small absorbance changes. (iii) The possibility of changing the length of the light path through the solution without having to change the size and shape of the titration vessel. (v) Also desirable are the characteristics of stability, linearity of response, simplicity of electric circuitry, independence of cell configuration, and continuous selection of wavelength.

Several differences are noted between the instrumental requirements for a phototitrator and those for a photometer. Important among these is the matter of stability. A phototitrator must provide information on the change in absorbance of a solution after successive additions of titrant over a prolonged period of time. During this period the zero and 100 per cent transmittance (T) points must be constant. Photometers on the other hand normally function by comparison of the absorbance of a sample solution with that of a reference solution within the time span of a few seconds. (In a double beam instrument the comparison is essentially continuous.) Knowledge of the exact location of the zero and 100 per cent T points is required in a photometric determination; a requirement which can frequently be relaxed in a titration. The requirement of full reproducibility of pathlength necessary for a photometric determination is also relaxed in a phototitration for which only consistence over the course of a titration is required. Similar considerations apply to wavelength. Further, operation in ambient light, of considerable practical importance

in a phototitrator, is of little advantage in a photometer.

There are two principle approaches which permit operation in ambient light. The first is the use of chopped light to create an alternating current signal at the detector. This signal is electronically separated from the direct current component due to ambient light. The circuitry required is usually quite involved and, for a simple titrator, prohibitively expensive. One rather simple instrument of moderate cost utilizing this design approach is commercially available, namely, the Spectrosyn Colorimeter[44] which is described below.

The second approach to exclusion of ambient light is based on exclusion by geometry. Several instruments of this design have been reported and are described below.

Flaschka and Sawyer[42] were able to successfully cope with the problem of ambient light and thus construct an instrument designed to be a phototitrator free of the worst of the problems previously hampering practical application of the principles of photometric titrations. In their instrument, a rather weak beam of nearly parallel light passes through the solution and enters the detector compartment through an interference filter. The beam is then focussed on an extremely small photodetector. Ambient light is excluded on geometrical grounds; the angle subtended by the lamp housing being greater than the maximum angle of acceptance of the detector system. Ambient light scattered by the titration vessel or solution is greatly attenuated by passage through the filter, and the stray light actually reaching the detector is found to be negligible.

In a later instrument, Flaschka and Butcher[43] refined the design of the phototitrator by incorporating an immersible probe for the introduction of light into the sample solution. Ambient light is still excluded by geometry. Two advantages were evident in the new design. First, the requirement for an optical cell was relaxed since the "semi-immersion" titrator required only a container with an optical bottom. Second, a variable pathlength feature was added.

Several full-immersion instruments have been described so far in the literature. Agazzi and Bond[45] reported on a design in which two tubes are immersed into the solution. One tube contains the light source near the immersed end. A beam from this source passes through the solution to the immersed end of the other tube which contains the photoreceptor. A filter can be positioned in the light path to select the appropriate wavelength. The length of the light path is fixed, the light probe is sizable, and thus titrations of small samples become difficult.

Recently Muto and co-workers[5] reported on a "dipping colorimeter." The path length is fixed, glass filters are used to achieve monochromacy and external light must be excluded.

The phototitrator by Fisher[46] immerses two light conducting glass rods into the solution. Light exits from one rod, passes through a gap filled with the solution to be titrated, enters the other rod and is brought by it to the detector. The path length is invariable as in the preceding instrument, and some modification of ambient light level is necessary. However, the use of an interference filter wedge, which allows continuous selection of the wavelength, is an improvement.

The best of the instruments so far described is the Spectrosyn Electronic Colorimeter[44] which employs the chopped light principle. The light probe in this instrument is of quite small diamter and contains a small bulb enclosed in a cylindrical stainless-steel housing. This lamp housing and a second cylinder containing the photoreceptor are mounted on a steel rod. The light housing can be moved axially relative to the receptor compartment and thereby a path length between 0 and 5 cm can be adjusted. The lamp is operated by a current pulsating at a frequency of 33.3 cycles per second. The signal due to the modulated light is isolated electronically from that due to the external light and rectified by a lock-in amplifier circuit. The resulting direct current signal is displayed on a meter that reads in per cent transmittance. Thus, external light need not be excluded. Monochromacy is achieved by small, specially mounted filters that are slipped onto the front plate of the detector housing. Continuous wavelength variation is not possible. The instrument is line operated and thus subject to the voltage fluctuations in the line. Isolation of the alternating current component in the detector output and rectification requires moderately sophisticated electronic circuitry. However, two desirable features of an ideal phototitrator, namely, variable path length and independence of ambient light, are fulfilled in this design. An instrument of this type has been in use in the present author's laboratory for several years, and has performed extremely well as a phototitrator. The limited precision (one per cent transmittance as given by the manufacturer) and influence of moderate line voltage fluctuations are not overly serious in titrations, in which the multitude of readings take provides an error reducing averaging process.

Design and Construction

Consideration of and experimentation with a number of possible designs for photometric titrators convinced the author that although the instruments described above perform well within their limitations, still much room was left for improvement. In particular, previous instruments constructed in this laboratory had been compromise designs. Each had fallen short of the goals of complete independence of cell configuration and continuous wavelength selection. About six months was spent in preliminary investigations of components and designs with the hope of combining the best features of each of the existing instruments. In particular the performance of the Spectrosyn Colorimeter described above, encourage the author to attempt to develop a low cost electric circuit for use in conjunction with a chopped light beam. In the final analysis, the cost of the electronics required was not consistent with the cost of the other systems envisioned for the instrument, so this approach was abandoned. In addition, a study was conducted to determine the feasibility of using fiber optics for a portion of the optical system. The fiber system was quickly abandoned because of the high losses associated with collimation of the emerging beam.

The immediate result of the deliberations and experimentation described above was the decision to persue a design based on geometrical exclusion. It was also possible at this point to recognize five design features desired in the proposed new design. They are:

1. Variable path length
2. Continuous selection of wavelength
3. Independence of ambient light
4. Simplicity of electric circuitry
5. Independence of cell configuration

Points 1, 3, and 4 had all been achieved in previous instruments built in this laboratory. Their incorporation in the design was then only a matter of utilization of proven principles. Solution of the remaining points without compromising the others required some development.

The decision to use geometrical exclusion of ambient light provided the route to solution to point 3 since application of the principle had been demonstrated using a photodetector of extremely small sensitive area in previous designs. The application of such a detector automatically solved point 4, since a quite simple circuit consisting of only a few batteries, resistors and switches can be employed. Point 2 was solved by abandoning filters and operating with a grating. The construction of this portion of the optical part of the titrator was greatly facilitated by employing the collimating system and the grating with its drive mechanism from a Bausch and Lomb Spectronic 20 no longer in service. (If such a source is not at hand the parts can be purchased for less than 50 dollars.) Development of an uncomplicated light probe that allows variation of the path length presented the greatest difficulties in design and construction.

The general lay-out of the instrument is shown in the optical schematice (Figure 9). The light source, S, is a General Electric #209 automotive lamp. Light from the source is collimated by the lens assembly, B. This unit was taken intact from a Bausch and Lomb Spectronic 20, and consists of two lenses and a slit which serves as entrance slit for the monochromator. The collimated beam is reflected by a mirror, Q, down the probe assembly, P, which ends in a glass window. A second-surface mirror, M, is positioned in the sample solution below the end of the tubu-

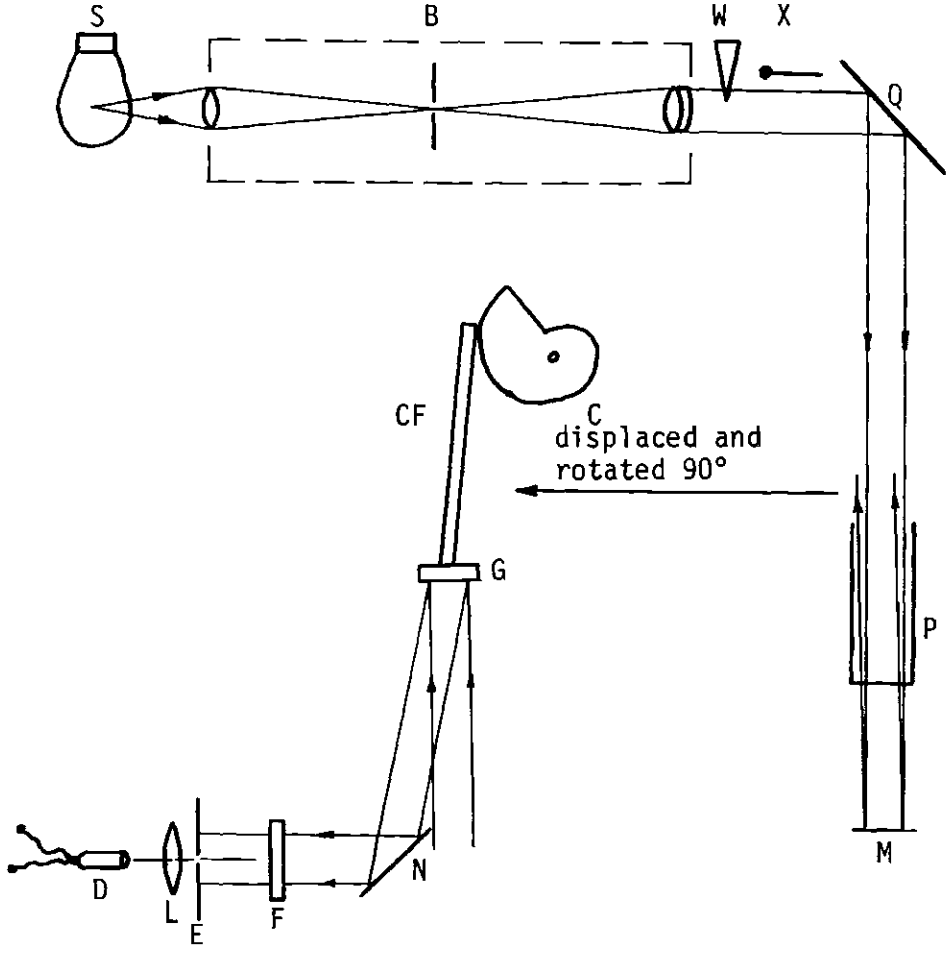

Figure 9. Optical Schematic Diagram of the Photometer.

lar probe. The light, after exiting the probe, is reflected by M back into the probe at an angle of 5.5°. When the probe assembly is submerged into a solution, the light beam returning to the probe from M, has traversed the solution with a path length of essentially twice the distance between the surface of the end window and the front surface of the mirror, M.

After having crossed the sample gap and traversed the tube again the light beam strikes a diffraction grating, G. This is a replica grating taken from a Bausch and Lomb Spectronic 20. It has been remounted to conform to the geometry of the optical path, but is driven by the cam, C, and cam follower, CF, which accompany it in the Spectronic 20. This grating was selected for its low cost and proven performance. It should be noted that the optical schematic (Figure 9) has been drawn with the optical path broken and the grating and following optics displaced and rotated 90° from their orientation in the instrument. The diffracted light is directed by mirror N through an infra-red filter, F, to the monochromator exit slit, E. Then the light is focussed by lens, L, on detector, D.

The detector is a Texas Instrument 1N2175 symmetrically diffused silicon photo-duo-diode, which is particularly suited for this application because of its small size and limited angle of acceptance of incident light. The device is only 12 mm in length by 2 mm in diameter. The light sensitive area is less than one square millimeter. The extremely small angle of acceptance for incident light is achieved by a lens which comprises the open end of the detector. The light sensitive semi-conductor chip is located at the focal point of this lens. Light off the optical

axis misses the chip entirely. The spectral sensitivity of the device is adequate throughout most of the visible range but falls very rapidly at wavelengths below 420 nm. This fact, combined with reduced energy output by the light source at the lower wavelengths, severely curtails exploitation of the near-ultraviolet region. The detector has its maximum sensitivity at about one micron. The high sensitivity in this region makes necessary the infra-red filter, F, which serves to eliminate the effect of lower order spectra produced by the grating. Recently, a Texas Instrument LS-400 silicon photo-duo-diode has been used which is physically similar to the 1N2175, but has about ten times greater sensitivity.

Two control devices are included in the optical path; a shutter, X, to completely block the light beam, both as protection for the detector, and as zero transmittance reference, and a comb, W, for fine adjustments of the intensity of the incident light.

The titrator is completely contained in an aluminum box especially assembled for the purpose. The physical dimensions are 20 x 20 x 45 cm. The box is divided down the long dimension into two compartments. One half contains the optical components, the other the electric circuitry. All control functions are grouped on or near the front panel for ease of operation. To facilitate repair and adjustment, the top, side and rear panels of the box are demountable and the front panel consists of two sections of which the right one is hinged. Connections to the galvanometer and exciter battery are made through pronged plugs mounted on the rear of the case. It should be emphasized at this point that no attempt has been made to optimize the cabinet configuration. On the contrary, the container employed was built for maximum flexibility during design

evolution. When in use, the instrument rests on a four-legged aluminum rack. This positions the titrator with the probe assembly several centimeters above the bench top, allowing room for a beaker and stirrer.

Figure 10 shows the arrangement of optical components in the box. The source, S, is mounted on a stage which has facility for adjustments in three dimensions. The source on the stage can also be axially rotated to achieve proper position of the lamp filament. Screw drive is provided for these adjustments, and set screws allow locking. The collimating system, B, is permanently attached to the frame of the box as are the mounts for all other optical components. Controls for comb, W, and shutter, X, are located on the side near the front of the box. The comb is driven by a worm gear, and the shutter is operated by a brass rod. Adjusting screws are provided for the optical alignment of mirrors Q and N as well as the stage for mirror, M. Alignment of detector, D, is also possible.

Detector, D, collimating lens, L, exit slit, E, and infra-red filter, F, are mounted as a unit in an aluminum block, DE. The details of this unit are shown in the inset of Figure 10. The permanent alignment of this group of components facilitates instrument alignment. In addition, the massive aluminum mount serves as a heat sink for the photoreceptor.

The probe assembly used for photometric titrations (see Figure 10) consists of a 15 mm outer diameter glass tube closed with a glass window at the lower end, and mounted in a 25 mm brass sleeve. The sleeve in turn fits snugly into an aluminum block which is secured to the phototitrator frame. Also mounted in this block are four stainless steel rods. These extend parallel to the probe, and below it, to the corners of a 3 cm square stainless steel plate on which is mounted the mirror, M. The size of the

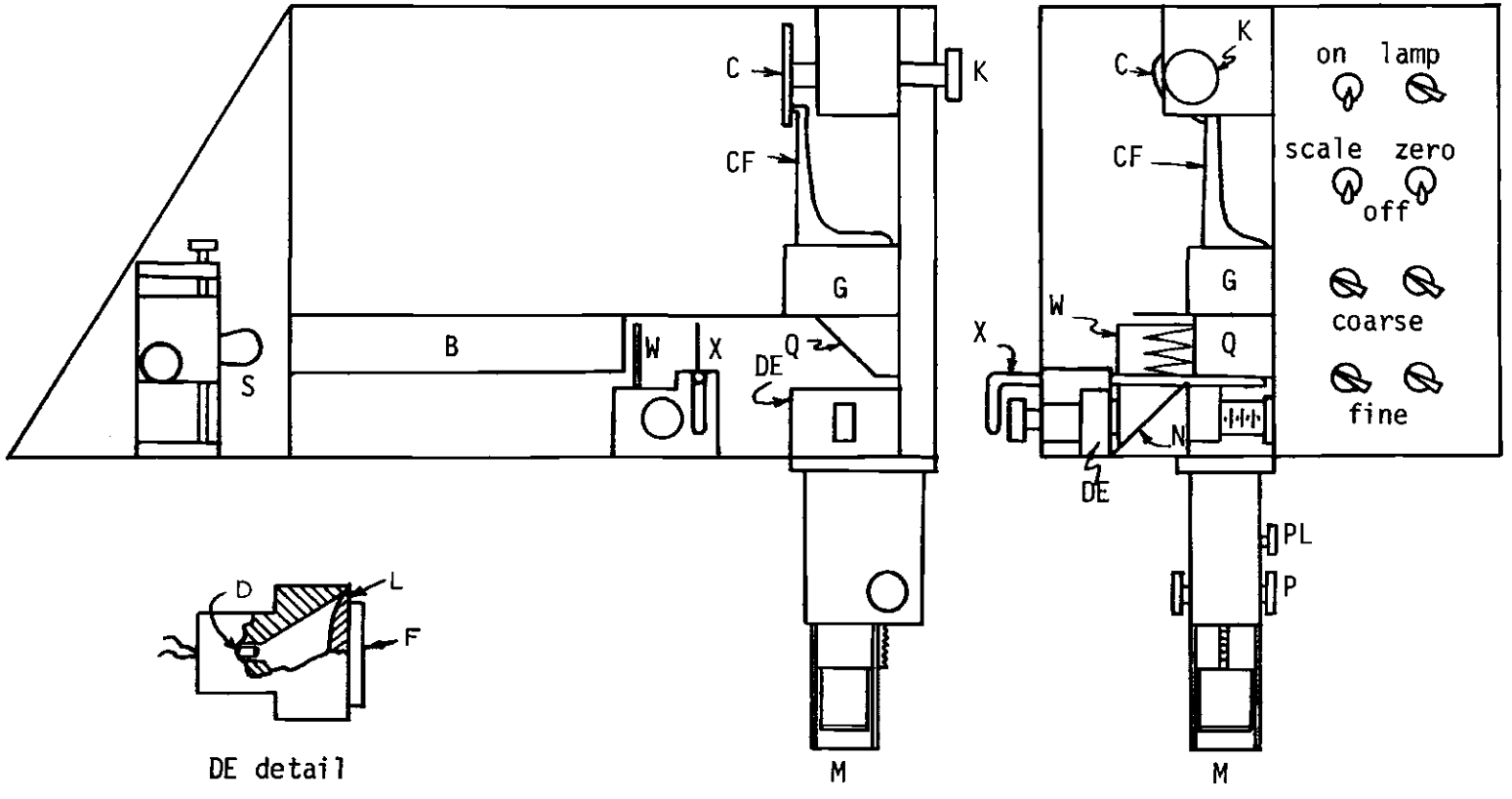

Figure 10. General View of the Photometer.

stage is ample to accommodate both the stage mirror (12 x 9 mm) and a small magnetic stirring bar. The exposed portions of the stage and the support rods may be Teflon coated. The mounting of the support rods allows their exposed length to be adjusted and kept by set screws. Rough alignment of the optical path is achieved by adjusting stage orientation. Precise alignment is accomplished using mirrors Q and N.

Variation of the pathlength is achieved by driving the sleeve and the attached dipping glass tube with a rack and pinion gear. The rack is secured to the sleeve and the pinion gear to the mount. A locking set screw, PL, is provided. The range of the probe drive is about 5 cm which allows continuous path length adjustment from 0 to 10 cm. Longer path lengths are possible by extending the stage legs.

The wavelength is set using knob K which drives the cam and thereby rotates the grating. A wavelength scale viewed through a window in the non-hinged portion of the front panel is attached to the cam shaft. (Scale and front panel are not shown in Figure 10.)

The electric circuit employed (shown schematically in Figure 11) is similar to those used in previous designs.[42,43,48] It will be noted that the circuit is basically a series arrangement of photodetector, detector power supply, and output device. The particular circuit shown is designed for use with a Rubicon galvanometer. The model selected has a sensitivity of about 0.0006 μA/mm over the 100 mm scale, an internal resistance of about 4.5 kiloohms, and a critical damping resistance of about 85 kiloohms. In order to assure linear response of the 1N2175 the resistance of all components in series with the detector have been kept as low as possible.

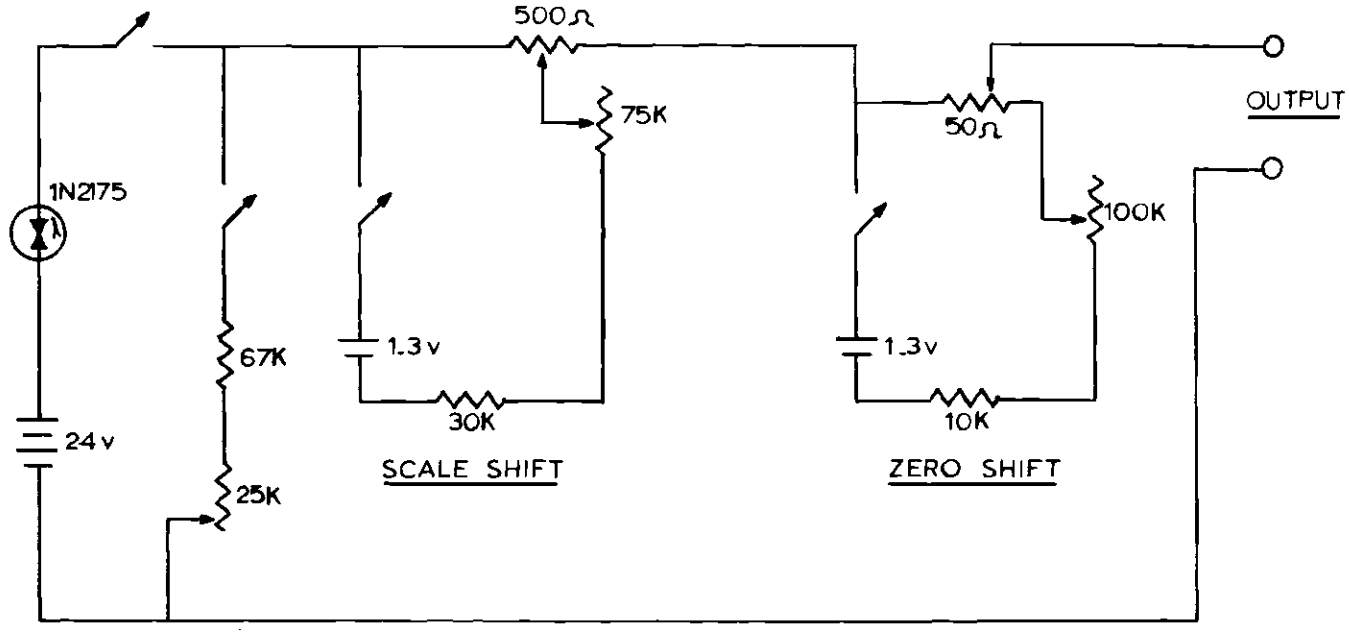

Figure 11. Schematic Diagram of the Electric Circuit of the Photometer.

The batteries shown in the circuit are mercury cells. Two 12-volt batteries are used as the main source; 1.34-volt cells are used in the control circuits.

The zero shift circuit provides a simple method of adjusting the galvanometer to zero thereby compensating for the dark current. Fine adjustment of this circuit involves changing the resistance of the cell circuit; however, this change has a negligible effect on the damping behavior and sensitivity of the galvanometer and the sensitivity of the detector and the linearity of its response. Operation with the scale expanded to the right (beyond 100 %T) is readily possible by appropriate adjustment of the light intensity. The scale shift circuit provides the much needed additional capacity of expanding the scale to the left (below zero %T). The circuit yields up to about 400 scale divisions of shift without affecting the linearity of response.

The current drain in both circuits (zero shift and scale shift) is extremely small.

The exciter lamp is actuated by a step switch which permits selection of either 2, 4, or 6-volt operation, and thereby coarse adjustment of the light intensity. Fine adjustment is achieved by using the comb, W. The step voltages are provided by two six volt lead storage batteries connected in parallel and tapped by cells. Two batteries are required, since at six volts the lamp draws around 1.25 amps.

Performance Tests

A tuning procedure is used to calibrate the grating. An interference filter is placed in the optical path, the knob, K, is set at the

wavelength of the filter, and the cam follower is adjusted for maximum detector output. No resetting of the cam follower was necessary when verifying the calibration at several additional wavelengths, thus indicating proportionality between the linear scale and the wavelength.

The linearity of response and the stability of the entire instrument were tested by the methods previously described.[43] Linearity up to an absorbance of about 0.8 was demonstrated. No short term fluctuations were noted, and long term drift did not exceed 0.2 scale divisions per hour. Linearity was also confirmed in case the instrument was used with recorder output.

The effectiveness of exclusion of ambient light was demonstrated by illuminating the probe assembly with a 100-watt tungsten bulb. No deviations in instrument reading could be detected.

Application

The utility of the full-immersion design for a phototitrator has been demonstrated by routine use in the author's laboratory. The instrument has satisfied the design criteria of simplicity, ease of operation, versatility, ruggedness, stability, and low cost. Photometric titrations have been conducted both manually and automatically. For the latter purpose a Sargent Recorder and a constant flow buret were used.

Although the original intention was to construct a phototitrator, the instrument described here can equally well be used as a photometer, which shows the advantages of freedom from restrictions on ambient light conditions and cell configuration. In fact the photometer functions with the ruggedness, and simplicity normally associated with a modern pH meter,

and is used in much the same manner. The probe is first immersed in a reference solution for "calibration" of the scale, then after brief rinsing, the probe is dipped in the test solution. Any beaker or other vessel large enough to accommodate the light probe can be used.

Exactly reproducible adjustment of a certain path length is difficult with the variable path length probe, although not impossible with the application of a caliper. However, for analytical purposes the majority of the cases do not require such an adjustment. Normally, a determination is made within the rectilinear portion of the calibration curve, that is, in the range where Beer's Law is obeyed. Then, all that is needed is an approximate reproduction of the path length and one calibrating measurement on a standard solution. Thus, the variable path length probe can be used in photometric determination although with limitation. However, it is not difficult to construct probe assemblies with invariable and precise light path. Several of such designs have been built and tested. The following one proved to be most convenient. A glass tube is closed at its lower end by a glass plate. Sections of the tube extend below the window to support a mirror. The spacing between the mirror surface and the window is set at exactly one half of the desired path lengths. The upper end of the tube is mounted in a brass cylinder which is secured to the body of the instrument by a bayonet fitting thus allowing ready interchange of probes of different path lengths.

The full-immersion instrument in a special application allowed the solution of an aggravating problem, in an amazingly simple manner. Time studies of reactions in the cooled solutions encountered in the cobalt analysis described in Chapter IV. To perform such photometric studies

with a common photometer is quite difficult because special arrangements are necessary to avoid fogging of the cuvette containing the cold liquid. Even with appropriate aspiration of dry air along the cuvette, difficulties exist because the relatively small amount of solution in the cuvette possesses insufficient heat capacity to maintain the low temperature. With the light tube of the immersion photometer sealed also at its upper end (after filling with a dry gas) by gluing on a thin plate of glass, no fogging occurs. When dipped into a cold solution maintaining the desired temperature was no longer a problem because the vessel containing the test solution could simple be immersed in a cooling solution.

Operation

The operation of the instrument is analogous whether employed as a photometer or a photototitrator. The essential difference is that for photometer operation usually an exact setting of 100 %T is necessary while for titrator operation the upper limit can be any value appropriate for the case at hand. However, this difference is sufficient to warrant a separate description of operational details, as given below.

One special feature of the design is the capacity for scale expansion by zero suppression (that is, scale shift to the left). The potential gain in precision associated with scale expansion has been discussed in Chapter II. Since this feature can be employed in either of the two uses of the instrument, the procedure of programming a 100-division shift will be described first.

Programming for Zero Suppression

Select any wavelength, attach any probe assembly and set zero with

the scale shift circuit off. To set zero close shutter, X, activate the zero shift circuit and operate its controls to bring the pointer exactly to the zero mark. Next set 100 %T as follows. Open the shutter, X, and select (by turning the step switch) a lamp voltage that gives the minimum light intensity for at least full scale deflection. Then bring the pointer from the 100 mark back to exactly the zero mark. The instrument is now programmed. In any later operation (provided, of course, the respective controls remain untouched) if the scale shift circuit is activated, the pointer will be shifted 100 scale division to the left.

With the instrument programmed as described the effective zero is at -100 scale divisions. The pointer may now be moved back to the 100 mark by operating the lamp step switch or the comb or both. The range between zero and 100 %T is then 200 scale divisions, of which, however, only the upper half is displayed. If, during the later operation of the instrument, the pointer moves below the zero mark, deactivation of the scale shift circuit displays the lower half of the 200 scale division range.

Zero suppression for 200 and more scale divisions (up to a total of 400) is possible. However, suppression by 100 scale division was found sufficient for all present purposes of the instrument and no attempt was made to incorporate the necessarily more complicated circuit for higher suppressions.

Photometer Operation

First set the desired wavelength and path length. The latter may be accomplished either by attaching the appropriate fixed-path-length

probe or by attaching the variable-probe assembly and adjusting it to the required path length. Set zero as described above. Set 100 %T as described above but with the probe immersed in the reference solution. Remove the vessel containing the reference solution, immerse the probe into the sample solution and read per cent transmittance. Zero suppression may be employed as needed.

Titrator Operation

Two principal cases may be differentiated. A down-scale titration in which the pointer moves left (that is, to lower transmittance values) as the titration proceeds, and an up-scale titration in which the opposite takes place.

Down-scale titrations. Select the desired wavelength, set zero and attach the variable probe assembly with the appropriate path length adjusted. Immerse the probe into the sample solution completely readied for the titration and bring the pointer to the 100-mark by operating the lamp step switch or the comb or both. Start adding titrant and take readings after addition of each increment and plot the data as usual. Selection of the optimum path length may be difficult if not known from prior experience with a particular titration system. In such an event a test titration with an aliquot of the sample solution may be performed. The probe is immersed, the pointer brought near the 100-mark and excess titrant is added. Thus, the range of pointer movement is readily established. If only a limited amount of sample solution is avaiable the titration may be performed with about half of the sample solution, the path length adjusted according to this portion of the titration and then the rest of the solution added and the titration finished.

Increased sensitivity may be secured by utilizing the zero suppression as described above.

Up-scale titration. This type of titration is somewhat more difficult than the preceding one because it requires specific knowledge of the position of the pointer at or past the end point. It is, of course, possible to operate in the following way. Set zero as usual and 100 %T with the solvent as the reference. Then the pointer will definitely stay on scale during the titration but the capability of the instrument to yield highest sensitivity is not utilized. It is better to adjust the 100-mark with an over-titrated solution. When doing so, lamp step switch, comb and above all the variability of the path length should be employed in conjunction, to achieve the optimum range of pointer movement. It should be noted that actually the adjustment is not made to the 100-mark but rather to 95 or even 90 scale divisions in order to allow for the decrease in transmittance due to dilution effects during the titration. Alternative adjustment to the 100-mark may be made and if the pointer passes beyond that mark the scale shift circuit (correctly programmed for 100 scale divisions) may be activated to bring the pointer back on scale.

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*Abbreviations used herein follow the form shown in "Index of Periodicals," Chemical Abstracts, 1956.

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VITA

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